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

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The hydrolysis of $Al(^tBu)_3$ in toluene using the hydrated salt $Al_2(SO_4)_3{\cdot}14H_2O$ 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 $[(^tBu)_2Al(\mu\text{-}OH)]_3{\cdot}n\text{MeCN}$ (n = 1(**3**), 2) and $[(^tBu)_2Al(\mu\text{-}OH)]_3{\cdot}2\text{THF}$, 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 pentaaluminum 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. The low-temperature thermolysis of $[(^tBu)_2Al(\mu\text{-}OH)]_3$ in pentane yields $[(^tBu)Al(\mu_3\text{-}O)]_6$ as the major product and allows for the isolation of a possible precursor to the hexamer, the "basket" structured $[Al_6(^tBu)_8(\mu_3\text{-}O)_4(\mu\text{-}OH)_2]$ (**6**). When it is heated, compound **6** is readily converted into $[(^tBu)Al(\mu_3\text{-}O)]_6$ with concomitant liberation of isobutane. Reaction of $[(^tBu)_2Ga(\mu\text{-}OH)]_3$ with $Al(^tBu)_3$ in toluene yields $Ga(^tBu)_3$ and the octameric alumoxane $[(^tBu)Al(\mu_3\text{-}O)]_8$ (**7**) as the major isolable products. Mass spectrometry indicates the incorporation of low levels of gallium (<8%) into samples of **7** made by this route. A topological relationship for the prediction of the structures of "closed" cage alumoxane compounds $[(^tBu)Al(\mu_3\text{-}O)]_n$ is suggested: the stable structures of $[(^tBu)Al(\mu_3\text{-}O)]_n$ will have six four-membered Al_2O_2 rings and $n - 1$ six-membered Al_3O_3 rings. This relationship is discussed with respect to the known structures for main-group clusters with $n = 4{-}12$. The molecular structures of compounds **2**, **4**, **6**, and **7** have been determined by X-ray crystallography. Crystal data for **2**: monoclinic, $P2_1/c$, a = 10.012(6) Å, b = 9.426(3) Å, 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) Å, b = 11.337(2) Å, c = 20.143(4) Å, β = 97.84(3)°, Z = 4, R = 0.054, R_w = 0.055. Crystal data for **6**: triclinic, $P\bar{1}$, a = 10.343(5) Å, b = 11.776(8) Å, c = 19.45(1) Å, α = 100.05(1)°, β = 94.64(1)°, γ = 107.15(1)°, Z = 2, R = 0.102, R_w = 0.122. Crystal data for **7**: monoclinic, $C2/c$, a = 19.831(7) Å, b = 12.980(7) Å, c = 19.753(5) Å, β = 103.20(4)°, Z = 8, R = 0.047, R_w = 0.0053.

Introduction

We have recently reported[2] the first conclusive evidence that alkylalumoxanes, prepared by the hydrolysis of AlR_3, have the general formula $(RAlO)_n$. On the basis of spectroscopic evidence, confirmed by the X-ray crystallographic structural determinations 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 of 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 in both 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.

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(2) Mason, M. R.; Smith, J. M.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1993**, *115*, 4971.

(3) MAO is the commonly used acronym for methylalumoxane; however, PMAO (poly(methylalumoxane)) is also used by several commercial vendors.

(4) Pasynkiewicz, S. *Polyhedron* **1990**, *9*, 429.

(5) For a review of group 13−16 clusters see: Barron, A. R. *Comments Inorg. Chem.* **1993**, *14*, 123.

(6) For a comprehensive review on cage compounds of main group metals, see: Veith, M. *Chem. Rev.* **1990**, *90*, 3.

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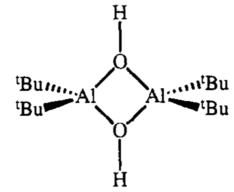
Results and Discussion

Hydrated Salt *versus* Direct Hydrolysis of $Al(^tBu)_3$. We have previously reported[2] that the direct reaction of $Al(^tBu)_3$[7] with 1 molar equiv of water results in the liberation of isobutane 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, 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 0.5 equiv of water had apparently reacted with $Al(^tBu)_3$. While hydrated aluminum sulfate is sold as the octadecahydrate, $Al_2(SO_4)_3{\cdot}18H_2O$,[8] thermogravimetric analysis (TGA) of a commercially available sample indicated that only 14 (±1) waters of hydration are in fact present. Thus, a less than stoichiometric quantity of water was available for reaction with $Al(^tBu)_3$. This realization has prompted us to reinvestigated the hydrated-salt hydrolysis of $Al(^tBu)_3$.

The addition of $Al(^tBu)_3$ to a suspension of $Al_2(SO_4)_3{\cdot}14H_2O$ in toluene followed by heating to reflux yields the dimeric aluminum hydroxide $[(^tBu)_2Al(\mu\text{-}OH)]_2$ (**1**) (eq 1). Unlike its trimeric analog, compound **1** does not decompose in the solid state at room temperature under an inert atmosphere.

$$Al(^tBu)_3 \xrightarrow{\frac{1}{14}Al_2(SO_4)_3\cdot 14H_2O} \tfrac{1}{2}[(^tBu)_2Al(\mu\text{-}OH)]_2 + {}^tBuH \quad (1)$$

The presence of a hydroxyl group in compound **1** is substantiated by a singlet ^1H NMR resonance at 1.12 ppm and a $\nu(OH)$ stretch (3697 cm^{-1}) in the infrared spectrum. The hydroxide resonance in the ^1H 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 peaks in the mass spectrum due to $M^+ - H$ and $M^+ - {}^tBu$ (see Experimental Section). While X-ray crystallographic data was obtained for compound **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 compound **1**.



I

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 an equilibrium mixture of trimers and dimers.[10] 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 are 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.[10] The same principles appear 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 is observed. Addition of H_2O to a toluene solution of $Al(^tBu)_3$, heated to reflux (*Caution: This reaction is extremely violent*; see Experimental Section), 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 trimers $[Me_2Al(\mu\text{-}OR)]_3$ resulted in their conversion to the corresponding dimers (eq 2). However,

$$2[Me_2Al(\mu\text{-}OR)]_3 \underset{t_{1/2}\ ca.\ weeks,\ 25\ °C}{\overset{t_{1/2}\ ca.\ min,\ 110\ °C}{\rightleftharpoons}} 3[Me_2Al(\mu\text{-}OR)]_2 \quad (2)$$

the alkoxide dimer is slowly converted to the trimer (eq 2) upon reequilibration ($t_{1/2} \approx 2-3$ months). As we have previously reported, heating the hydroxide trimer $[(^tBu)_2Al(\mu\text{-}OH)]_3$ results in its conversion to the alumoxanes; however, if the thermolysis is carried out on a sufficiently large scale (>50 g), then the ^1H 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 $[(^tBu)_2Al(\mu\text{-}OH)]_2$ to $[(^tBu)_2Al(\mu\text{-}OH)]_3$.

Unlike $[(^tBu)_2Al(\mu\text{-}OH)]_3$, compound **1** is not readily converted to alumoxanes upon thermolysis. Whereas $[(^tBu)_2Al(\mu\text{-}OH)]_3$ eliminates alkane even at room temperature, compound **1** shows no reaction until heated in refluxing decane (174 °C) for 15 h. In this regard compound **1** is similar to $[(^tBu)_2Ga(\mu\text{-}OH)]_3$, which requires refluxing in xylene (143−145 °C) to enable conversion into $[(^tBu)Ga(\mu_3\text{-}O)]_9$.[11] However, unlike $[(^tBu)_2Ga(\mu\text{-}OH)]_3$, thermolysis of **1** yields a mixture of alumoxanes, $[(^tBu)Al(\mu_3\text{-}O)]_n$ (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 isobutane is an intramolecular reaction, then the distance and orientation between the hydroxide proton and the α-carbon of the *tert*-butyl

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[7] (a) Uhl, W. *Z. Anorg. Allg. Chem.* **1989**, *570*, 37. (b) Lehmkuhl, H.; Olbrysch, O.; Nehl, H. *Justus Liebigs Ann. Chem.* **1973**, 708.(c) Lehmkuhl, H.; Olbrysch, O. *Justus Liebigs Ann. Chem.* **1973**, 715.

[8] Strem Chemicals Catalog No. 93-1350.

[9] Bott, S. G., personal communication.

[10] Rogers, J. H.; Apblett, A. W.; Cleaver, W. M.; Tyler, A. N.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1992**, 3179.

[11] Power, M. B.; Ziller, J. W.; Barron, A. R. *Organometallics* **1992**, *11*, 2783.

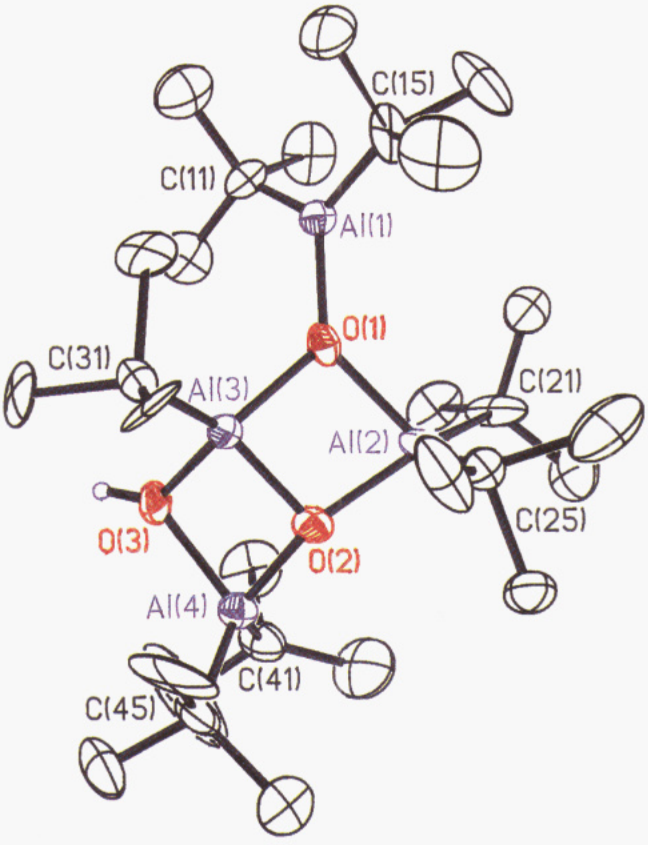

Figure 1. Molecular structure of $[\text{Al}_4(^t\text{Bu})_7(\mu_3\text{-O})_2(\mu\text{-OH})]$ (**2**). Thermal ellipsoids are drawn at the 30% level, and the hydrogen atoms of the *tert*-butyl groups are omitted for clarity. Only the major component of the disorder is shown (see Experimental Section).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $[\text{Al}_4(^t\text{Bu})_7(\mu_3\text{-O})_2(\mu\text{-OH})]$ (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)−Cl(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)

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 downfield 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 those in estimating hydroxide acidity. However, while the hydroxide proton–*tert*-butyl α-carbon distance in $[(^t\text{Bu})_2\text{Al}(\mu\text{-OH})]_3$ can be determined from X-ray crystallography (3.49 Å), the lack of good structural data for $[(^t\text{Bu})_2\text{Al}(\mu\text{-OH})]_2$ 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 $[(^t\text{Bu})_2\text{Al}(\mu\text{-OH})]_2$ can be made from the calculated structure of $[\text{H}_2\text{Al}(\mu\text{-OH})]_2$ (3.69 Å).[10] The validity of this estimate can be ascertained by comparing the value obtained experimentally for the flat Al_3O_3 cycle of $[(^t\text{Bu})_2\text{Al}(\mu\text{-OH})]_3$ and the values of the axial substituents in $[\text{H}_2\text{Al}(\mu\text{-OH})]_3$ (3.51 Å),[10] which is calculated to adopt a chair conformation. The values for $[(^t\text{Bu})_2\text{Al}(\mu\text{-OH})]_3$ and $[\text{H}_2\text{Al}(\mu\text{-OH})]_3$ are clearly larger than that for $[(^t\text{Bu})_2\text{Al}(\mu\text{-OH})]_2$. Furthermore, the orientation between the hydroxide and the *tert*-butyl group, 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) is estimated to be approximately 69.5° for **1** and determined to be 33° for $[(^t\text{Bu})_2\text{Al}(\mu\text{-OH})]_3$. 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 $[(^t\text{Bu})_2\text{Al}(\mu\text{-OH})]_3$ and $[(^t\text{Bu})_2\text{Ga}(\mu\text{-OH})]_3$ would be expected to be similar, which they are not.

As noted above, compound **1** is the major product isolated from the salt hydrolysis of $\text{Al}(^t\text{Bu})_3$, while $[(^t\text{Bu})_2\text{Al}\{\mu\text{-OAl}(^t\text{Bu})_2\}]_2$ 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 tetraaluminum product, $[\text{Al}_4(^t\text{Bu})_7(\mu_3\text{-O})_2(\mu\text{-OH})]$ (**2**). The ^{1}H and ^{13}C NMR spectra 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 1. 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) is 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 is 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 1) 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 $[(^t\text{Bu})_2\text{Al}\{\mu\text{-OAl}(^t\text{Bu})_2\}]_2$. As can be seen from Scheme 1, hydrolysis of $[(^t\text{Bu})_2\text{Al}\{\mu\text{-OAl}(^t\text{Bu})_2\}]_2$ followed by com-

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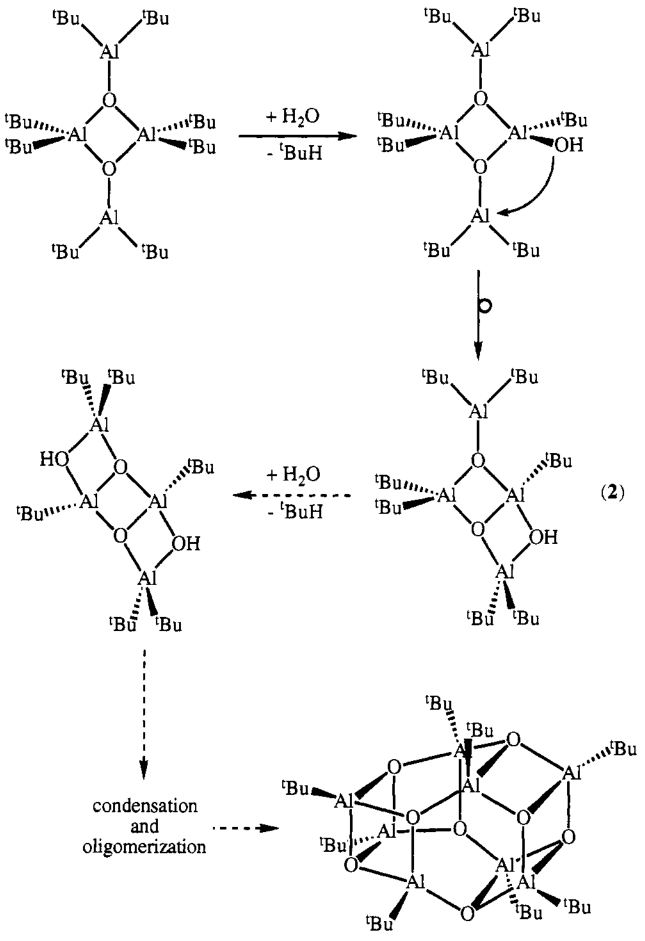
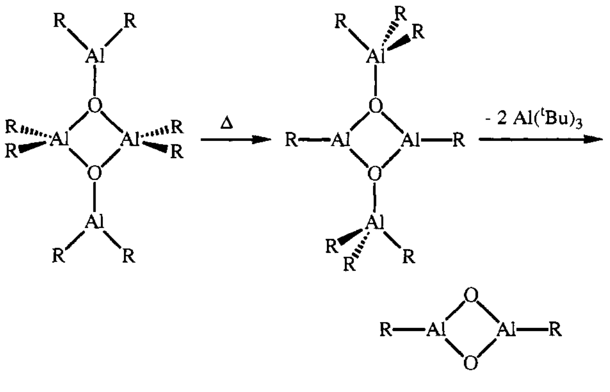
[12] Apblett, A. W.; Warren, A. C.; Barron, A. R. *Chem. Mater.* **1992**, *4*, 167.

Scheme 1. Proposed Reactions Responsible for the Formation of Compound 2 and [(^{t}Bu)Al(μ_3-O)]$_8$ during the Salt Hydrolysis of Aluminum Alkyls, Al(^{t}Bu)$_3$



(2)

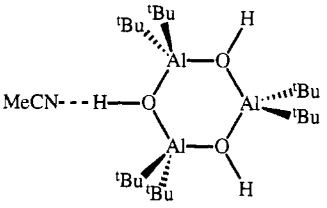
plexation of one of the three-coordinate aluminum centers with the hydroxide yields compound **2**. Furthermore, as shown in Scheme 1, additional hydrolysis of compound **2** may explain the formation of [(^{t}Bu)Al(μ_3-O)]$_8$, which was previously observed to be formed as a side product with [(^{t}Bu)$_2$Al{μ-OAl(^{t}Bu)$_2$}]$_2$, but not upon the thermolysis of [(^{t}Bu)$_2$Al(μ-OH)]$_3$.[2] On the basis of literature precedent, we have previously assumed that the small quantity of [(^{t}Bu)Al(μ_3-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$_2$Al(μ-OAlMe$_2$)]$_2$ to yield (MeAlO)$_n$.[19] However, the isolation of compound **2** would suggest that our previous isolation of [(^{t}Bu)Al(μ_3-O)]$_8$ was actually due to the nonstoichiometric hydrolysis conditions employed (see above).



(3)

Reaction of [(^{t}Bu)$_2$Al(μ-OH)]$_2$ with Lewis Bases. Recrystallization of [(^{t}Bu)$_2$Al(μ-OH)]$_2$ from MeCN yields [(^{t}Bu)$_2$Al(μ-OH)]$_3$ as the main product; further cooling of the supernatant yields crystals of [(^{t}Bu)$_2$Al(μ-OH)]$_2$·MeCN (**3**). In contrast, removal of the excess MeCN from a solution of [(^{t}Bu)$_2$Al(μ-OH)]$_2$ yields [(^{t}Bu)$_2$Al(μ-OH)]$_3$·2MeCN.[2] Compound **3** may also be isolated by stirring equimolar quantities of [(^{t}Bu)$_2$Al(μ-OH)]$_3$ and [(^{t}Bu)$_2$Al(μ-OH)]$_3$·2MeCN in hexane. Recrystallization of **1** from THF yields the previously reported solvate [(^{t}Bu)$_2$Al(μ-OH)]$_3$·2THF.[2]

The IR spectrum of **3** shows two ν(OH) bands, one due to a free hydroxide (3585 cm^{-1}) and a broad band with increased intensity for the hydrogen-bonded hydroxide (3259 cm^{-1}). The ^{1}H 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 previously reported by us for a MeCN:Al ratio 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(μ-NR'$_2$)]$_n$.[13] The only difference in the present case is the solvation of the hydroxide by the Lewis base.

Compound **3** slowly decomposes in the solid state at room temperature to yield [(^{t}Bu)Al(μ_3-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 [(^{t}Bu)Al(μ_3-O)]$_6$ as the major alumoxane species formed during the thermolysis of [(^{t}Bu)$_2$Al(μ-OH)]$_3$.[2] Similarly, the presence of MeCN during the hexane thermolysis of **1** or [(^{t}Bu)$_2$Al(μ-OH)]$_3$ results in the formation of the nonamer [(^{t}Bu)Al(μ_3-O)]$_9$ in 50–60% yield.

Hydrolysis of Al(^{t}Bu)$_2$(^{i}Bu). Like other workers,[7] we have found that the synthesis of Al(^{t}Bu)$_3$ from AlCl$_3$ and *tert*-butyllithium results in the formation of Al(^{t}Bu)$_2$(^{i}Bu) as a sometimes significant side product. The factors controlling the relative yield of Al(^{t}Bu)$_3$ and Al(^{t}Bu)$_2$(^{i}Bu) are unclear; however, we have observed that once Al(^{t}Bu)$_3$ is prepared in the absence of Al(^{t}Bu)$_2$(^{i}Bu) then the former does not rearrange to the latter,

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(13) Sauls, F. C.; Czekaj, C. L.; Interrante, L. V. *Inorg. Chem.*, **1990**, *29*, 4688.

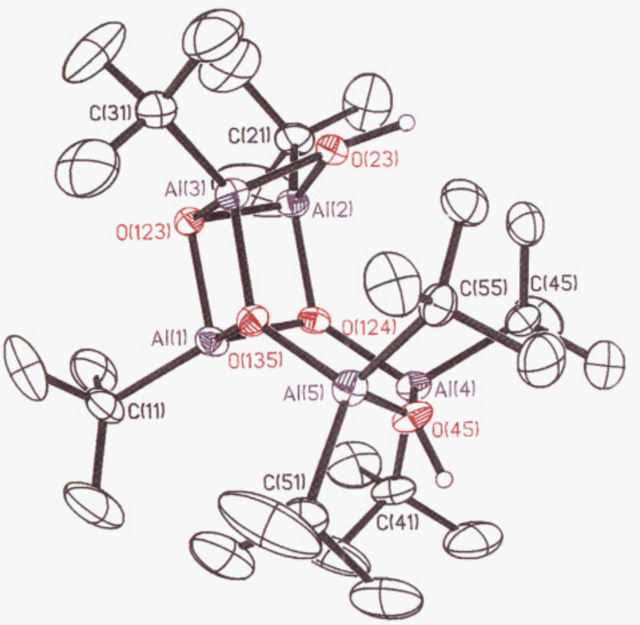


Figure 2. Molecular structure of [$Al_5(^tBu)_7(\mu_3\text{-}O)_3(\mu\text{-}OH)_2$] (**4**). Thermal ellipsoids are drawn at the 40% level, and the hydrogen atoms of the *tert*-butyl groups are omitted for clarity.

suggesting that the *tert*-butyl to isobutyl 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 $Al(^tBu)_2(^iBu)$, at −78 °C, results in the high-yield formation of $[(^tBu)_2Al(\mu\text{-}OH)]_3$. There is no evidence for the formation of the alternative product $[(^tBu)(^iBu)Al(\mu\text{-}OH)]_n$, suggesting that the hydrolysis occurs with the least sterically hindered alkyl and not the weakest Al−C bond.

Isolation and Structural Characterization of New Pentameric and Heptameric Alumoxanes. In our original report of the synthesis of *tert*-butyl alumoxanes the thermolysis of $[(^tBu)_2Al(\mu\text{-}OH)]_3$ was carried out on the 3−5-mmol scale, allowing for the isolation of the three main products $[(^tBu)Al(\mu_3\text{-}O)]_6$, $[(^tBu)Al(\mu_3\text{-}O)]_9$, and $[(^tBu)Al(\mu_3\text{-}O)]_{12}$. If the reaction is carried out on a much larger scale (ca. 90 mmol), then two additional new compounds may be isolated in low yield along with a small quantity of the dimeric hydroxide, compound **1**, further supporting the temperature dependence of the hydrolysis reaction.

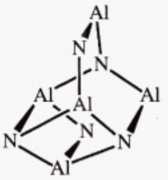
Thermolysis of a hexane solution of $[(^tBu)_2Al(\mu\text{-}OH)]_3$ yields a mixture of alumoxanes, of which the hexamer $[(^tBu)Al(\mu_3\text{-}O)]_6$ is the major product and from which, by repeated fractional crystallization, compound **4** may also be isolated. The ^1H and ^{13}C NMR spectra of **4** indicate the presence of seven aluminum-bound *tert*-butyl environments in a 1:2:2:2 ratio and two nonequivalent hydroxyl groups. The presence of two hydroxide environments is confirmed by IR spectroscopy: ν(OH) 3681 and 3599 cm^{-1}. The relative shifts of these bands are similar to those observed for **1** and $[(^tBu)_2Al(\mu\text{-}OH)]_3$, suggesting that the hydroxides are positioned within a four-membered Al_2O_2 and six-membered Al_3O_3 cycle, respectively (see below). The EI mass spectrum of **4** exhibits a fragment (*m/z* 559, 95%) consistent with the composition $Al_5{}^tBu_6O_5H_2$ (i.e., $M^+ - {}^tBu$). The analytical and spectroscopic characterization of compound **4** is consistent with a pentaaluminum compound, the structure of which has been determined by X-ray crystallography to be [$Al_5(^tBu)_7(\mu_3\text{-}O)_3(\mu\text{-}OH)_2$] (**4**).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [$Al_5(^tBu)_7(\mu_3\text{-}O)_3(\mu\text{-}OH)_2$] (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)
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)		

The molecular structure of compound **4** is shown in Figure 2; selected bond lengths and angles are given in Table 2. 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] The core structure of compound **4** is best considered to result from 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 isostructural with five-sevenths of the Ga_7S_7 heptameric structure we have previously reported for $[(^tBu)Ga(\mu_3\text{-}S)]_7$.[11]

III



IV

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

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(14) Perego, G.; Del Piero, G.; Cesari, M.; Zazzetta, A. Dozzi, G. *J. Organomet. Chem.* **1975**, *87*, 53.

(15) Perego, G.; Dozzi, G. *J. Organomet. Chem.* **1981**, *205*, 21.

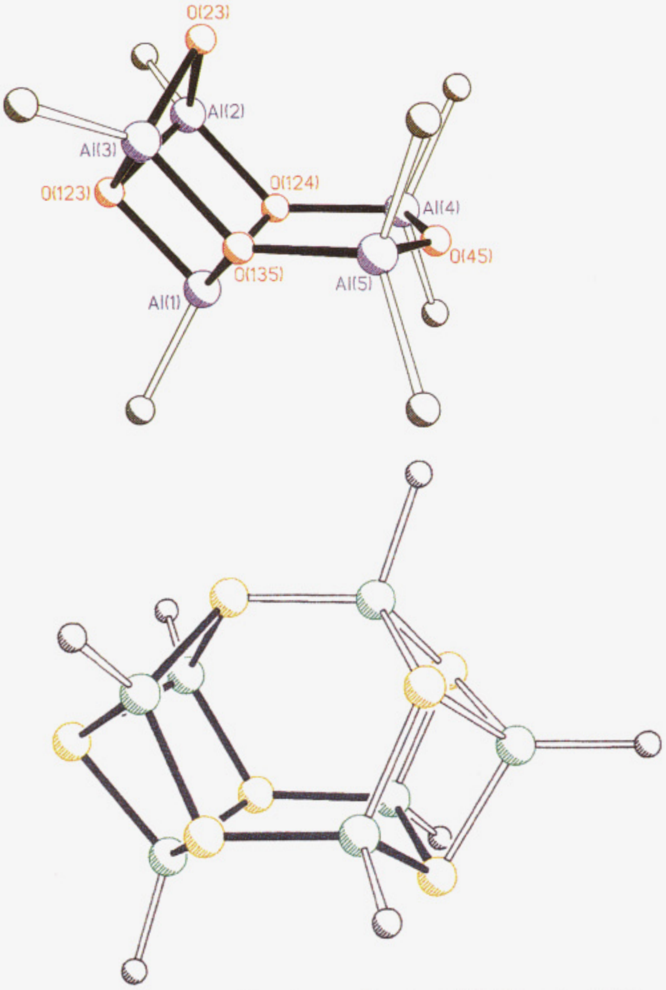

Figure 3. The core structures of (a, top) $[Al_5(^tBu)_7(\mu_3\text{-}O)_3(\mu\text{-}OH)_2]$ and (b, bottom) $[(^tBu)Ga(\mu_3\text{-}S)]_7$. The solid lines represent the common structural fragment present in **4** and **5**. Aluminum and gallium atoms are shown in purple and green, respectively.

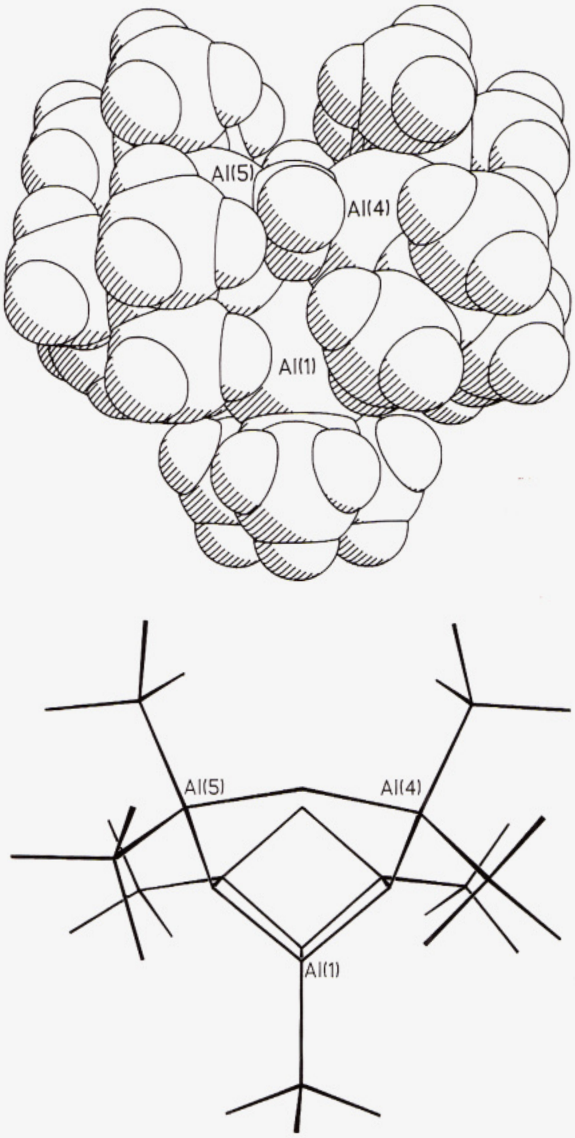

Figure 4. Space-filling representation of (top) $[Al_5(^tBu)_7(\mu_3\text{-}O)_3(\mu\text{-}OH)_2]$ (**4**) and (bottom) its equivalent line drawing, viewed perpendicular to the Al(1)−Al(4)−Al(5) plane, showing the steric hindrance imposed on Al(1) by the *tert*-butyl groups.

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 the geometry around Al(1). While the other aluminum centers are essentially tetrahedral, Al(1) is closer to trigonal bipyramidal: the *tert*-butyl C(11) and O(124) and O(135) occupy the pseudoequatorial ligand sites ($\Sigma[X{-}Al{-}X] = 357.1°$, compared to 360 and 328.5° for trigonal-bipyramidal and tetrahedral geometries, respectively), while the pseudoaxial 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 $[(^tBu)Al(\mu_3\text{-}O)]_6$ and $[Al_5(^tBu)_7(\mu_3\text{-}O)_3(\mu\text{-}OH)_2]$ by fractional crystallization from the large-scale hydrolysis of $[(^tBu)_2Al(\mu\text{-}OH)]_3$, the isolation of the heptameric alumoxane $[(^tBu)Al(\mu_3\text{-}O)]_7$ (**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 ^{1}H and ^{13}C NMR spectra (see Experimental Section) are analogous to those that we have previously observed for the gallium sulfide cage compound $[(^tBu)Ga(\mu_3\text{-}S)]_7$, with which compound **5** is most likely isostructural.

Structural Relationship of $[Al_5(^tBu)_7(\mu_3\text{-}O)_3(\mu\text{-}OH)_2]$ to Siloxy-Substituted Alumoxanes, Alumina Gels, and the Mineral Boehmite. We have previously demonstrated that, like $[(^tBu)Al(\mu_3\text{-}O)]_n$, non-alkyl alumoxanes such as those found in aluminum based sol-gels also have three-dimensional rather than two-dimensional structures. However, the alumoxanes do not have the general formula $[(X)AlO]_n$ ($X = OR, OSiR_3, O_2CR$) but possess a variable composition best represented by $[Al(O)_x(OH)_y(X)_z]_n$ ($2x + y + z = 3$). Furthermore, the core structure of these "sol-gel" type alumoxanes is not that of a closed cage but is related to that of the mineral boehmite, [Al(O)(OH)].[16] The structural characterization of compound **4** 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

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[16] See: Apblett, A. W.; Landry, C. C.; Mason, M. R.; Barron, A. R. *Mater. Res. Soc. Symp. Proc.* **1992**, *249*, 75 and references therein.

[17] Wefers, K.; Misra, C. *Oxides and Hydroxides of Aluminum*; Alcoa Laboratories, 1987.

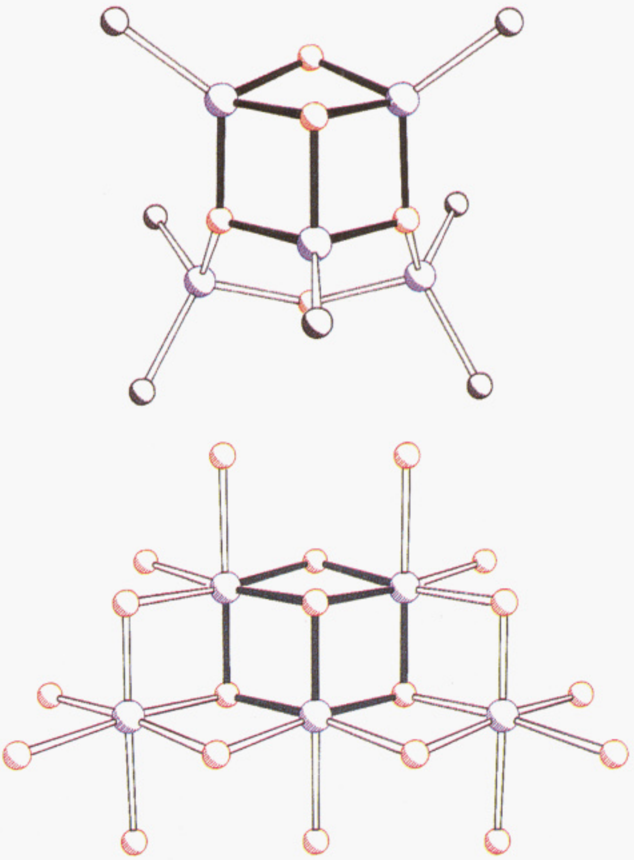


Figure 5. (a) Aluminum-oxygen core structure of $[Al_5(^tBu)_7(\mu_3\text{-}O)_3(\mu\text{-}OH)_2]$. The solid bonds represent the structural fragment present in the mineral boehmite. (b) Structure of boehmite. Aluminum atoms are shown in purple and oxygen in red.

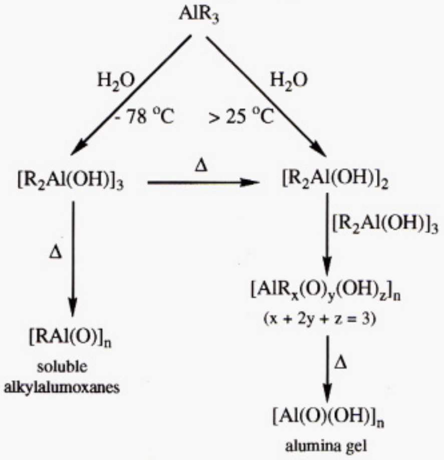
similarity between the core of compound **4** (Figure 5a) and the structure of boehmite (Figure 5b). Further evidence for this relationship is based on the observation that thermolysis of a toluene solution of compound **4** results in gel formation, from which a white powder may be obtained. The X-ray powder diffraction of this compound showed broad rings at d spacings (d = 6.11, 3.16, 2.34 Å) consistent with the 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). However, during the

$$AlR_3 \xrightarrow[-2RH]{+H_2O} RAlO \xrightarrow[-RH]{+H_2O} Al(O)(OH) \qquad (4)$$

synthesis of *tert*-butylalumoxanes, we have previously not observed any gel formation, leading us to question the relationship of our alkylalumoxanes to these alumina gels. On the basis of 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 cagelike 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.

Scheme 2. Proposed Reactions Responsible for the Formation of Soluble Alkylalumoxanes versus Alumina Gels during the Hydrolysis of Aluminum Alkyls, AlR_3



Low-Temperature Thermolysis of $[(^tBu)_2Al(\mu\text{-}OH)]_3$. If, as discussed above, the formation of the dimeric hydroxide $[(^tBu)_2Al(\mu\text{-}OH)]_2$ (**1**) during the thermolysis of $[(^tBu)_2Al(\mu\text{-}OH)]_3$ is a consequence of the reaction temperature, then presumably the formation of the former may be limited if the thermolysis of $[(^tBu)_2Al(\mu\text{-}OH)]_3$ is carried out at temperatures lower than that required for the trimer-to-dimer conversion.

Thermolysis of $[(^tBu)_2Al(\mu\text{-}OH)]_3$ in pentane at 35 °C is very slow (5–6 days); however, compound **1** is not detected among the reaction products. In addition to the major product, $[(^tBu)Al(\mu_3\text{-}O)]_6$, if the thermolysis is halted prior to completion (3 days) a new compound is observed to be present in the ^1H NMR spectrum of the reaction mixture in addition to traces of $[Al_5(^tBu)_7(\mu_3\text{-}O)_3(\mu\text{-}OH)_2]$. The new alumoxane, compound **6**, may be separated from $[(^tBu)Al(\mu_3\text{-}O)]_6$ and $[Al_5(^tBu)_7(\mu_3\text{-}O)_3(\mu\text{-}OH)_2]$ by repeated crystallization from hexane. The ^1H and ^{13}C NMR spectra of compound **6** indicate the presence of four sets of aluminum-bound *tert*-butyl environments in a 1:1:1:1 ratio and one hydroxyl group environment. The presence of the hydroxide moiety is confirmed by IR spectroscopy: $\nu(OH)$ 3610 and 3599 cm^{-1}. The relative ^1H NMR shift of the hydroxide resonance suggests that the hydroxides are positioned within a six-membered Al_3O_3 cycle. The EI mass spectrum of **6** exhibits a fragment ($M^+ - {}^tBu$, m/z 659, 50%) consistent with the composition $Al_6(^tBu)_8O_6H_2$. The analytical and spectroscopic characterization of compound **6** is consistent with a hexaaluminum compound of the formula $[Al_6(^tBu)_8(\mu_3\text{-}O)_4(\mu\text{-}OH)_2]$ (**6**). On the

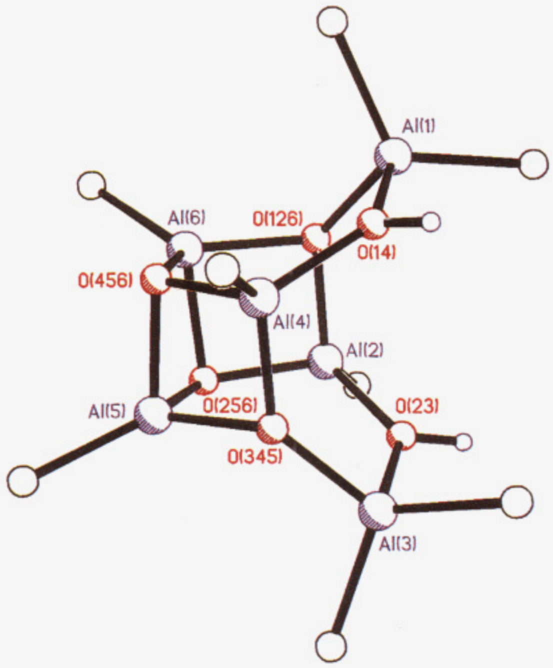
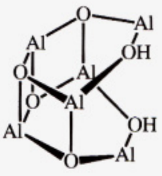


Figure 6. Molecular structure of [$Al_6(^tBu)_8(\mu_3\text{-}O)_4(\mu\text{-}OH)_2$] (**6**) (see Experimental Section). Methyl groups are omitted for clarity.

basis of the presence of four *tert*-butyl enviroments and a single hydroxide enviroment we have proposed compound **6** to have a core structure derived from the hexamer [$(^tBu)Al(\mu_3\text{-}O)]_6$ (**V**) by opening up of one of the four-membered faces, i.e., **VI**.

V



VI

While X-ray crystallographic data were obtained for **6**, problems with refinement precluded a detailed analysis of the structure (see Experimental Section). However, the solution was sufficient to confirm the atomic connectivity, and this is shown in Figure 6. The cage structure consists of two six-membered Al_3O_3 rings that are connected by four Al$-$O bonds. The aluminum and oxygen atoms not joining the two six-membered rings have two *tert*-butyl groups and a hydroxide hydrogen, respectively. The resulting structure may be likened to an aluminum$-$oxygen basket. The structure of compound **6** is wholly consistent with the solution spectra and mass spectrum.

An open cage structure similar to that of compound **6** was proposed for [$Al_6H_8(\mu_3\text{-}N^iPr)_4\{\mu\text{-}NH(^iPr)\}_2$]; however, no structural information was obtained due to the facile decomposition to [$(H)Al(\mu_3\text{-}N^iPr)]_6$.[18] It is possible, therefore, that compound **6** is the direct precursor to the hexameric alumoxane [$(^tBu)Al(\mu_3\text{-}O)]_6$. In fact, thermolysis of compound **6** (45 min, 80 °C) does lead to the quantitative formation of [$(^tBu)Al(\mu_3\text{-}O)]_6$ with isobutane as the only side product, suggesting that **6** is the direct precursor to [$(^tBu)Al(\mu_3\text{-}O)]_6$.

Reaction of [$(^tBu)_2Ga(\mu\text{-}OH)]_3$ with $Al(^tBu)_3$. We have previously reported the tetraalkyldialuminum alumoxane [$(^tBu)_2Al\{\mu\text{-}OAl(^tBu)_2\}]_2$ and suggested that it was formed as a result of the reaction of an aluminum hydroxide with $Al(^tBu)_3$. However, at this time attempts to isolate [$(^tBu)_2Al\{\mu\text{-}OAl(^tBu)_2\}]_2$ directly by 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, [$(^tBu)Al_xGa_{1-x}(\mu_3\text{-}O)]_n$.

Addition of $Al(^tBu)_3$ to a toluene solution of [$(^tBu)_2Ga(\mu\text{-}OH)]_3$[19] gives $Ga(^tBu)_3$ in near quantitative yield and a mixture of two aluminum-containing species, [$(^tBu)_2Al\{\mu\text{-}OAl(^tBu)_2\}]_2$ and [$(^tBu)Al(\mu_3\text{-}O)]_8$ (**7**), as the major (>60%) and minor (<5%) products, respectively. The ^1H and ^{13}C NMR spectra of compound **7** are consistent with our previously reported values for [$(^tBu)Al(\mu_3\text{-}O)]_8$; however, additional peaks are present, even in the samples used for X-ray crystallography. These resonances may be attributed to the presence of a second gallium-containing product as an impurity in **7** (see below).

The molecular structure of [$(^tBu)Al(\mu_3\text{-}O)]_8$ (**7**) is shown in Figure 7; selected bond lengths and angles are given in Table 3. The Al_8O_8 core can be described as being derived from the fusing of a hexameric cage and a square Al_2O_2 ring. A similar structure has been reported for the iminoalanes [$HAl(\mu_3\text{-}N^nPr)]_8$ and [$MeAl(\mu_3\text{-}NMe)]_8$.[20] 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 distances are in the region we have reported for aluminum μ_3-oxides.[2]

The EI mass spectrum of the crystal of compound **7** used for X-ray crystallographic determination exhibits a fragment (*m*/*z* 800, 100%) consistent with [$(^tBu)Al(\mu_3\text{-}O)]_8$; however, there are additional low-intensity signals due to [$(^tBu)_8Al_7Ga(\mu_3\text{-}O)_8$] and [$(^tBu)_8Al_6Ga_2(\mu_3\text{-}O)_8$] at *m*/*z* 842 (5%) and 884 (2%), respectively.[21] On the basis of ^1H NMR spectroscopy the total *tert*-butylgallium content may be estimated as *ca.* 8%. This 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 this content was not included in the final solution.

The formation of $Ga(^tBu)_3$ as the major gallium-containing product indicates that under the reaction conditions hydroxide exchange between gallium and aluminum occurs (eq 5) preferentially to the condensation elimination reaction between the gallium hydroxide and aluminum alkyl. Subsequent condensation of the aluminum hydroxide yields 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

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[18] Cucinella, S.; Salvatori, T.; Busetto, C.; Perego, G.; Mazzei, A. *J. Organomet. Chem.* **1974**, *78*, 185.

[19] Power, M. B.; Apblett, A. W.; Cleaver, W. M.; Ziller, J. W.; Barron, A. R. *Polyhedron* **1992**, *11*, 477.

[20] (a) Del Piero, G.; Cesari, M.; Perego, G.; Cucinella, S.; Cernia, E. *J. Organomet. Chem.* **1977**, *129*, 289. (b) Amirkhalili, S.; Hitchcock, P. B.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1979**, 1206.

[21] Values given for the ^{69}Ga isotope.

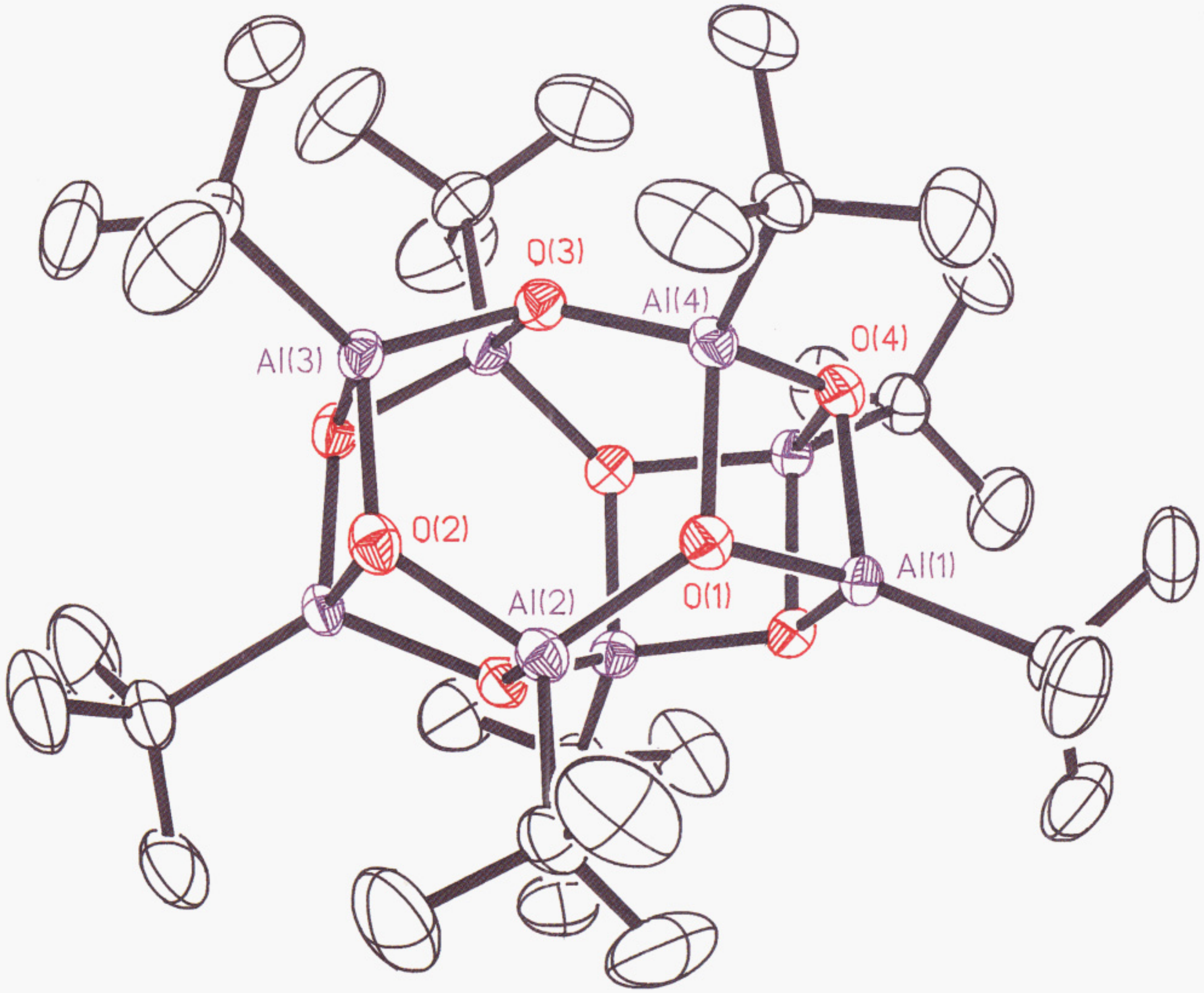

Figure 7. Molecular structure of $[(^tBu)Al(\mu_3\text{-}O)]_8$ (**7**). Thermal ellipsoids are drawn at the 30% level, and all the hydrogen atoms are omitted for clarity.

in eq 6) via compound **2** (*cf.* 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 (*cf.* eq 5) to give a *galloalumoxane*, the first to be reported.

$$Al(^tBu)_3 + {}^1/_3[(^tBu)_2Ga(\mu\text{-}OH)]_3 \rightarrow (1n)[(^tBu)_2Al(\mu\text{-}OH)]_n + Ga(^tBu)_3 \quad (5)$$

$$Al(^tBu)_3 + {}^1/_3[(^tBu)_2Al(\mu\text{-}OH)]_3 \rightarrow {}^1/_2[(^tBu)_2Al\{\mu\text{-}OAl(^tBu)_2\}]_2 + tBuH \quad (6)$$

Topological Structural Relationship for the Alumoxanes $[(^tBu)Al(\mu_3\text{-}O)]_n$, Gallium Sulfides $[(^tBu)Ga(\mu_3\text{-}S)]_n$, and Related Main-Group Cages. We have at this time isolated and characterized a wide range of alkylalumoxanes of the general formula $[(^tBu)Al(\mu_3\text{-}O)]_n$ ($n = 6, 7, 8, 9, 12$) as well as their gallium–sulfur analogs $[(^tBu)Ga(\mu_3\text{-}S)]_n$ ($n = 4, 6, 7, 8$). Furthermore, we have noted the analogy between the alumoxanes and the iminoalanes, whose structures are known for $[(R)Al(\mu_3\text{-}NR')]_n$ ($n = 4, 6, 7, 8$). On the basis of the structures observed for iminoalanes Smith[22] proposed that in stable cages the number of four-membered rings is constant (6) while the number of six-membered rings is dependent on the extent of oligomerization (i.e., n) and must be equal to $n - 4$. As would be expected, the alkylalumoxanes follow this rule; thus, the octameric compound **7** ($n = 8$) should consist of a cage with six four-membered Al_2O_2 faces, and four ($n - 4$) four-membered Al_3O_3 faces. This is indeed the structure observed (see above). We note that while all of the Al-N cages, as well as our Al-O and Ga-S compounds, structurally characterized thus far obey this rule, no prediction of the structures of cages larger than $n = 8$ was made by Smith, or subsequent workers,[23] due to the possibility of multiple isomers. However, from a consideration of the relationship between each of the isolated cages we propose that cages of increasing size are related by one of two possible growth relationships.

The smallest cage observed for the group 13–16 compounds is the cubane, i.e., $[(^tBu)Ga(\mu_3\text{-}S)]_4$. The simplest route to cage extension, from the structural rules laid down by Smith, would be addition of an M_2E_2

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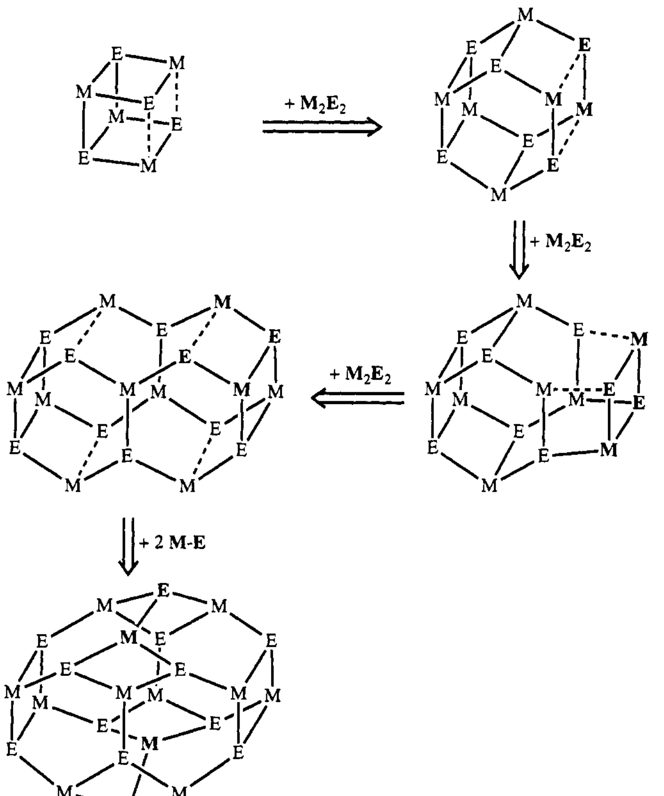
[22] Smith, J. D. Vortrag beim Anorganisch-chemischen Colloquium, Univ. München, **1974**, *25*, 7.

[23] Noth, H.; Wolfgardt, P. *Z. Naturforsch.* **1976**, *B31*, 697.

Table 3. Selected Bond Lengths (Å) and Angles (deg) of $[(^tBu)Al(\mu_3\text{-}O)]_8$ (7)

Al(1)−O(1)	1.817(3)	Al(1)−O(4)	1.878(3)
Al(1)−O(4a)	1.799(3)	Al(1)−C(1)	1.965(5)
Al(2)−O(1)	1.781(3)	Al(2)−O(2)	1.793(3)
Al(2)−O(3a)	1.856(3)	Al(2)−C(2)	1.939(5)
Al(3)−O(2)	1.800(3)	Al(3)−O(3)	1.817(3)
Al(3)−O(2a)	1.887(3)	Al(3)−C(3)	1.962(4)
O(1)−Al(1)−O(4)	85.7(1)	O(1)−Al(1)−O(4a)	108.1(1)
O(4)−Al(1)−O(4a)	88.0(1)	O(1)−Al(1)−C(1)	124.9(2)
O(4)−Al(1)−C(1)	122.1(2)	O(4a)−Al(1)−C(1)	118.3(1)
O(1)−Al(2)−O(2)	111.7(1)	O(1)−Al(2)−O(3a)	104.7(1)
O(2)−Al(2)−O(3a)	87.1(1)	O(1)−Al(2)−C(2)	115.2(2)
O(2)−Al(2)−C(2)	118.0(2)	O(3a)−Al(2)−C(2)	116.2(2)
O(2)−Al(3)−O(3)	107.3(1)	O(2)−Al(3)−O(2a)	87.8(1)
O(2a)−Al(3)−O(3)	85.5(1)	O(2)−Al(3)−C(3)	118.6(2)
O(2a)−Al(3)−C(3)	122.8(2)	O(3)−Al(3)−C(3)	125.0(2)
Al(1)−O(1)−Al(2)	124.7(1)	Al(1)−O(1)−Al(4)	92.7(1)
Al(2)−O(1)−Al(4)	126.6(1)	Al(2)−O(2)−Al(3)	126.0(2)
Al(2)−O(2)−Al(3a)	92.5(1)	Al(3)−O(2)−Al(3a)	92.8(1)
Al(3)−O(3)−Al(4)	125.1(2)	Al(3)−O(3)−Al(2a)	92.7(1)
Al(4)−O(3)−Al(2a)	126.9(1)		

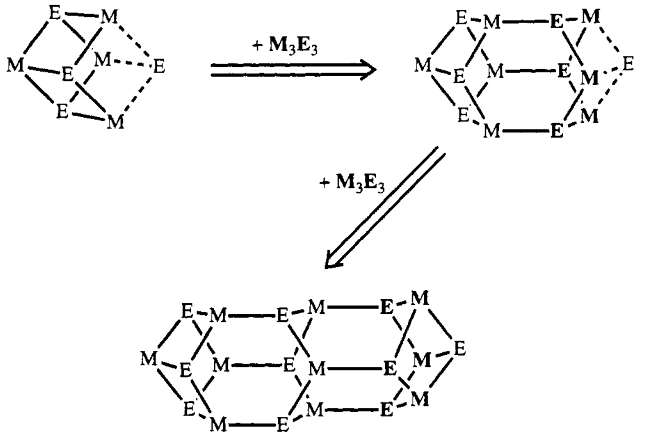
Scheme 3. Proposed Relationship between $[(^tBu)M(\mu_3\text{-}E)]_n$ (M = Al, Ga; E = O, S; n = 4, 6, 8,10)[a]



[a] Alkyl groups are omitted for clarity. The bold groups and the dashed lines represent respectively the M_2E_2 units added and the M−E bonds broken during the conceptual cage expansion.

(M = group 13 element, E = group 16 element) moiety to give the hexagonal prismane, $[(^tBu)M(\mu_3\text{-}E)]_6$. Subsequent additions would lead to the octamer and decamer (see Scheme 3). While there are no X-ray data for a decamer of this structure, the iminoalane decamer $[(H)Al(\mu_3\text{-}N^iPr)]_{10}$ has a ^1H NMR spectrum consistent with the presence of three imine environments in a 2:2:1 ratio that should be observed for such a structure and not the 1:3:3:3 ratio that should be observed for the alternative isomer (see below). Further cage expansion via the addition of two M−E units leads to the dodecamer structure observed for $[(^tBu)Al(\mu_3\text{-}O)]_{12}$.[2]

Scheme 4. Proposed Relationship between $[(^tBu)M(\mu_3\text{-}E)]_n$ (M = Al, Ga; E = O, S; n = 4, 7, 10)[a]



[a] Alkyl groups are omitted for clarity. The bold groups and the dashed lines represent respectively the M_2E_2 units added and the M−E bonds broken during the conceptual cage expansion.

The second cage expansion from the cube consists of insertion of an M_3E_3 cycle between one of the apexes and the remainder of the cube to give the heptamer and, subsequently, a second isomer of the decamer (see Scheme 4). The first example of a main-group cage compound with this decameric structure, $[(Et)Zn(\mu_3\text{-}SEt)]_{10}$, has been reported by Hampden-Smith and coworkers.[24]

We believe that these simple relationships outlined above can be used to predict the structures possible for alumoxanes and related main-group clusters for any extent of oligomerization. Furthermore, in combination with NMR spectral characterization a single isomer can be defined where more than one are possible.

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 (^1H, ^{13}C) or Bruker WM-300 (^{27}Al) spectrometers using (unless otherwise stated) benzene-d_6 solutions. Chemical shifts are reported relative to external TMS (^1H, ^{13}C) or aqueous $[Al(H_2O)_6)]^{3+}$ (^{27}Al).

All procedures were performed under purified nitrogen. Solvents were distilled and degassed prior to use. $Al(^tBu)_3$ and $[(^tBu)_2Ga(\mu\text{-}OH)]_3$ were prepared as previously reported.[7,19]

$[(^tBu)_2Al(\mu\text{-}OH)]_2$ (1). Method 1. $Al(^tBu)_3$ (4.3 g, 47 mmol) was added to a cooled (−78 °C) suspension of $Al_2(SO_4)_3{\cdot}14H_2O$ (1.9 g, 43 mmol of H_2O) in toluene (300 mL). The mixture was stirred at −78 °C for 1 h and was then warmed to room temperature. Stirring was continued at room temperature for 2 h. The mixture was refluxed for 15 h, cooled, and filtered. The filtrate was concentrated *in vacuo* to approximately one-third of its original volume and was stored at −20 °C for 2 days. A crude white crystalline product was isolated and recrystallized (2.1 g): isolated crystalline yield 31%.

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[24] Zeng, D.; Hampden-Smith, M. J.; Duesler, E. N. *J. Am. Chem. Soc.*, in press.

Table 4. Summary of X-ray Diffraction Data

	$[Al_4(^tBu)_7(\mu_3\text{-}O)_2(\mu\text{-}OH)]$ (**2**)	$[Al_5(^tBu)_7(\mu_3\text{-}O)_3(\mu\text{-}OH)_2]$ (**5**)
empir formula	$C_{28}H_{64}Al_4O_3$	$C_{28}H_{65}Al_5O_5$
cryst size, mm	0.40 × 0.35 × 0.30	0.31 × 0.35 × 0.31
cryst sist	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 = 0.710 73 Å), graphite monochromator	
temp, K	298	298
2*θ* range, deg	4.0–40.0	4.0–44.0
no. of rflns collected	5083	3737
no. of indep rflns	4759	3583
no. of obsd rflns	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, e Å^{-3}	0.65	0.32

	$[Al_6(^tBu)_8(\mu_3\text{-}O)_4(\mu\text{-}OH)_2]$ (**6**)	$[(^tBu)Al(\mu_3\text{-}O)]_8$ (**7**)
empir formula	$C_{32}H_{74}Al_6O_6$	$C_{32}H_{72}Al_8O_8$
cryst size, mm	0.23 × 0.24 × 0.10	0.52 × 0.46 × 0.61
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$C2/c$
a, Å	10.343(5)	19.831(7)
b, Å	11.776(8)	12.980(7)
c, Å	19.45(1)	19.753(5)
α, deg	100.05(1)	
β, deg	94.64(1)	103.20(4)
γ, deg	107.15(1)	
V, Å^3	2207(2)	7891.7(6)
Z	2	8
D(calcd), g cm^{-3}	1.079	1.005
μ, mm^{-1}	0.180	1.369
radiation	Mo Kα (λ = 0.710 73 Å) graphite monochromator	
temp, K	298	298
2*θ* range, deg	4.0–30.0	4.0–40.0
no. of rflns collected	2856	5276
no. of indep rflns	2640	5202
no. of obsd rflns	1197 ($\|F_o\| > 6.0\sigma(\|F_o\|)$	2680 ($\|F_o\| > 6.0\sigma(\|F_o\|)$
weighting scheme	$w^{-1} = \sigma^2(\|F_o\|) + 0.016(\|F_o\|)^2$	$w^{-1} = \sigma^2(\|F_o\|) + 0.04(\|F_o\|)^2$
R	0.102	0.047
R_w	0.122	0.053
largest diff peak, e Å^{-3}	0.59	0.22

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 $Al(^tBu)_3$ (23.7 g, 120 mmol) was added H_2O (2.15 mL, 120 mmol): mp 118 °C. Anal. Calcd for $C_8H_{19}AlO$: 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*H*), 1.08 (18H, s, C(C*H*$_3$)$_3$). ^{13}C NMR: *δ* 31.40 (C(*C*H$_3$)$_3$). ^{27}Al NMR: *δ* 132 ($w_{1/2}$ = 4090 Hz).

Table 5. Selected Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^3) for $Al_4(^tBu)_7(\mu_3\text{-}O)_2(\mu\text{-}OH)_2$ (2)

atom	*x*	*y*	*z*	*U*(eq)
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)
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)

$[Al_4(^tBu)_7(\mu_3\text{-}O)_2(\mu\text{-}OH)]$ (2). Fractional crystallization of the supernatant obtained in the synthesis of $[(^tBu)_2Al(\mu\text{-}OH)]_2$ (method 1) over a period of 6 weeks 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*H*), 1.23 (18H, s, C(C*H*$_3$)$_3$), 1.20 (18H, s, C(C*H*$_3$)$_3$), 1.06 (18H, s, C(C*H*$_3$)$_3$), 0.96 (9H, s, C(C*H*$_3$)$_3$). ^{13}C NMR: *δ* 31.57 (C(*C*H$_3$)$_3$), 30.89 (br, C(*C*H$_3$)$_3$), 30.13 (C(*C*H$_3$)$_3$).

$[(^tBu)_2Al(\mu\text{-}OH)]_3{\cdot}MeCN$ (3). Recrystallization of $[(^tBu)_2Al(\mu\text{-}OH)]_2$ from MeCN yields $[(^tBu)_2Al(\mu\text{-}OH)]_3$ upon crystallization. A second batch of solid may be obtained from further reduction of the supernatant. 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*H*), 1.28 (54H, s, C(C*H*$_3$)$_3$), 0.44 (3H, s, NCC*H*$_3$). ^{13}C NMR: *δ* 31.40 (C(*C*H$_3$)$_3$), 15.71 (*C*(CH$_3$)$_3$), −0.32 (NC*C*H$_3$).

Synthesis of $[Al_5(^tBu)_7(\mu_3\text{-}O)_3(\mu\text{-}OH)_2]$ (4) and $[(^tBu)Al(\mu_3\text{-}O)]_7$ (5). $[(^tBu)_2Al(\mu\text{-}OH)]_3$ (41 g, 87 mmol) was refluxed in 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 $[(^tBu)Al(\mu_3\text{-}O)]_6$ (*ca.* 4 g) and subsequent isolation of $[Al_5(^tBu)_7(\mu_3\text{-}O)_3(\mu\text{-}OH)_2]$ (*ca.* 0.7 g, 2.7%) and $[(^tBu)Al(\mu_3\text{-}O)]_7$ (*ca.* 0.5 g, 2%).

$[Al_5(^tBu)_7(\mu_3\text{-}O)_3(\mu\text{-}OH)_2]$ (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*H*), 1.72 (1H, s, O*H*), 1.27 (9H, s, C(C*H*$_3$)$_3$), 1.18 (18H, s, C(C*H*$_3$)$_3$), 1.11 (18H, s, C(C*H*$_3$)$_3$), 1.10 (18H, s, C(C*H*$_3$)$_3$). ^{13}C NMR: *δ* 32.0 (C(*C*H$_3$)$_3$), 31.7 (C(*C*H$_3$)$_3$), 30.1 (C(*C*H$_3$)$_3$), 29.3 (C(*C*H$_3$)$_3$).

$[(^tBu)Al(\mu_3\text{-}O)]_7$ (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*H*$_3$)$_3$), 1.21 (27H, s, C(C*H*$_3$)$_3$), 1.17 (27H, s, C(C*H*$_3$)$_3$). ^{13}C NMR: *δ* 29.81 (3C, C(*C*H$_3$)$_3$), 29.73 (1C, C(*C*H$_3$)$_3$), 27.80 (3C, C(*C*H$_3$)$_3$).

$[Al_6(^tBu)_8(\mu_3\text{-}O)_4(\mu\text{-}OH)_2]$ (6). A pentane solution (300 mL) of $[(^tBu)_2Al(\mu\text{-}OH)]_3$ (16 g, 33 mmol) was heated at reflux for 3

Table 6. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^3) for [$Al_5(^tBu)_7(\mu_3\text{-}O)_3(\mu\text{-}OH_2)$] (5)

atom	*x*	*y*	*z*	*U*(eq)
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)
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)

days. The ^{1}H NMR spectra of the reaction mixture indicated that *ca.* one-third of the trimer was still present. The pentane solution was concentrated to *ca.* 100 mL and cooled (−24 °C). A quantity of colorless crystals was isolated, which was determined to be a mixture of **6** and [$Al_5(^tBu)_7(\mu_3\text{-}O)_3(\mu\text{-}OH)_2$]. Further recrystallization from hexane (15 mL) at −10 °C gave pure **6** (ca. 50 mg, 0.5%). MS (EI): *m*/*z* 659 ($M^+ - {}^tBu$, 50%), 601 ($M^+ - {}^tBu - {}^tBuH$, 75%), 543 ($M^+ - 2{}^tBuH - {}^tBu$, 100%). IR (cm^{-1}): 3610 (m), 3599 (m), 1013 (s), 998 (s), 816 (s), 794 (s), 759 (s), 715 (s). ^{1}H NMR: δ 2.71 (2H, s, OH), 1.25 (18H, s, $C(CH_3)_3$), 1.15 (18H, s, $C(CH_3)_3$), 1.12 (18H, s, $C(CH_3)_3$). ^{13}C NMR: δ 31.3 ($C(CH_3)_3$), 31.2 ($C(CH_3)_3$), 30.6 ($C(CH_3)_3$), 30.4 ($C(CH_3)_3$).

Conversion of [$Al_6(^tBu)_8(\mu_3\text{-}O)_4(\mu\text{-}OH)_2$] to [$(^tBu)Al(\mu_3\text{-}O)]_6$. [$Al_6(^tBu)_8(\mu_3\text{-}O)_4(\mu\text{-}OH)_2$] (15 mg, 0.021 mmol) was heated in toluene-d_8 at 80 °C for 45 min. The ^{1}H NMR spectrum of the sample showed only [$(^tBu)Al(\mu_3\text{-}O)]_6$ and $HCMe_3$.

Reaction of [$(^tBu)_2Ga(\mu\text{-}OH)]_3$ with $Al(^tBu)_3$. A solution of $Al(^tBu)_3$ (2.8 g, 14.1 mmol) in toluene (10 mL) was added to a cooled (−78 °C) solution of [$(^tBu)_2Ga(\mu\text{-}OH)]_3$ (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 ^{1}H NMR spectrum was consistent with a mixture of $Ga(^tBu)_3$ and [$(^tBu)_2Al\{\mu\text{-}OAl(^tBu)_2\}]_2$. Removal of all the volatiles and recrystallization from toluene yielded further crystals of [$(^tBu)_2Al\{\mu\text{-}OAl(^tBu)_2\}]_2$ and a few large crystals of [$(^tBu)Al(\mu_3\text{-}O)]_8$. MS (EI): *m*/*z* 829 ($Al_6Ga_2(^tBu)_7O_8$, 2%), 800 ($8M^+$, 5%), 785 ($Al_7Ga(^tBu)_7O_8$, 30%), 743 ($8M^+ - {}^tBu$, 100%). ^{1}H NMR: δ 1.23 (36H, s, $C(CH_3)_3$), 1.18 (36H, s, $(CH_3)_3$).

Table 7. Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2 × 10^2) for [$(^tBu)Al(\mu_3\text{-}O)]_8$ (7)

	x	*y*	*z*	*U*(eq)^a
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)	3898(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)	2946(3)	5116(5)	6020(3)	117(3)
C(43)	2786(3)	3253(5)	6155(3)	113(3)

^{a} Equivalent isotropic *U*, defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Crystallographic Studies. Crystals of compounds **2**, **5**, **6**, and **7** 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 and unit cell and space group determination were all carried out in a manner previously described in detail.[25] The structures were solved using the direct methods program XS,[26] which readily revealed the positions of the Al, O, and 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 maps either revealed some of the hydrogen atom positions. However, organic hydrogen atoms were placed in calculated positions (U_{iso} = 0.08 Å^2; $d(C-H)$ = 0.96 Å) for refinement. Neutral-atom scattering factors were taken from the usual source.[27] Refinement of positional and anisotropic thermal parameters led to convergence (see Table 4). Final atomic positional parameters are given in Tables 5–7.

After the successful location of the Al, O, and C atoms in the structural refinement of compound **2**, a second molecule of [$Al_4(^tBu)_7(\mu_3\text{-}O)_2(\mu\text{-}OH)$] 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.

A lattice determination using both the P3 and XCELL programs suggested a triclinic cell for compound **6**. This was

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[25] Healy, M. D.; Wierda, D. A.; Barron, A. R. *Organometallics* **1988**, *7*, 2543.

[26] Nicolet Instruments Corp., Madison, WI, 1988.

[27] *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. 4.

confirmed by the lack of any systematic extinction or any diffraction symmetry other than the Friedel conditions. The two possible triclinic space groups are the noncentrosymmetric $P1$ and the centrosymmetric $P\bar{1}$. With $Z = 2$ and no expectation of a chiral molecule, the latter centrosymmetric space group would seem more probable and was later found to be the correct choice. Initial attempts to solve the structure in $P\bar{1}$ did not provide a chemically reasonable result. However, all of the aluminum, oxygen, and carbon atom positions for two molecules were readily revealed in $P1$ by the use of direct methods. From this initial solution it was clear that the Al_6O_6 cores are related by a center of symmetry; therefore, the solution was transformed from $P1$ to $P\bar{1}$. Despite the location and isotropic refinement of all the non-hydrogen atoms, the R factor of 0.102 and the high esd's for some bond distances and angles could not be further reduced. The poor diffraction of the crystal (no significant peaks were observed above 25°) and the subsequently inferior quality of the diffraction data did not allow for the anisotropic refinement of the structure. However, since all the chemically equivalent structural parameters are within experimental error of each other and, most importantly, previously reported values, and the structure is wholly consistent with the NMR spectroscopic data, this solution is undoubtedly correct. In addition, since only atom connectivity is important in the present case we do not believe the high esd's and R factors detract from the overall result.

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Supplementary Material Available: Listings of all bond lengths and angles and anisotropic thermal parameters for **2**, **4**, and **7** and a table of positional and isotropic thermal parameters for the second molecule of **2** (24 pages). Ordering information is given on any current masthead page.

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