

Structural Characterization of $\text{Al}_{10}\text{O}_6\text{Bu}_{16}(\mu\text{-H})_2$, a High Aluminum Content Cluster: Further Studies of Methylaluminoxane (MAO) and Related Aluminum Complexes

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The first structurally characterized isobutyl-containing aluminoxane compound is presented. The $\text{Al}_{10}\text{O}_6\text{Bu}_{16}(\mu\text{-H})_2$ (I) cluster is produced from neat octakis-isobutyltetraluminoxane ($\text{Al}_4\text{O}_2\text{Bu}_8$) at 80 °C in 6–8 h followed by slow crystallization. The crystal is triclinic (space group $P\bar{1}$) with the molecule lying on an inversion center. This aluminoxane contains both nearly linear, $154(2)^\circ$, aluminum-bridging hydrides and three-coordinate aluminum sites. Solid-state ^{27}Al magic-angle spinning (MAS) NMR experiments were done at 19.6 and 40 T (833 MHz and 1.703 GHz, ^1H) and at 30–35 kHz spinning speeds, leading to the determination of the C_q and η values for the two four-coordinate Al sites and a lower limit of C_q for the three-coordinate Al site. Geometry-optimized restricted Hartree–Fock calculations at the double- ζ level of an idealized structure (methyl substituted, D_{2h} geometry) yielded C_q and η in close agreement with experiment; C_q agrees within 3 MHz.

Introduction

Methylaluminoxane (MAO) has been the activator of choice for metallocene related catalysts, a new generation of single site catalysts revolutionizing polyolefin synthesis.^{1,2} Interestingly, the molecular structure(s) of MAO is unknown. Given that uncertainty, a strong need exists for well-characterized aluminoxanes as either structural models for MAO, spectroscopic references, or replacements for MAO. Although a number of well-characterized aluminoxanes with sterically encumbered alkyl groups have already been reported, it is highly desirable to extend the modeling study

to isobutyl analogues which are less bulky (thereby more MAO-like) and can be synthesized from commercially available, inexpensive triisobutylaluminum. Herein, we report the crystal structure and NMR spectra, both calculated and experimental, for a novel isobutylaluminoxane cage containing both bridging hydride sites and three-coordinate aluminum sites.

The controlled reaction of water with aluminum alkyls leading to numerous complex structures has a long history.^{1,3,4} For trimethylaluminum, hydrolysis yields MAO, a complex system with, as yet, unknown structure(s).^{1,2} Controlled hydrolysis of tri-*tert*-butylaluminum with water or hydrated metal salts leads to cage-type structures with four-coordinate aluminum sites bound to oxygen and one or more alkyl groups.^{5,6} Cages consisting of six, seven, eight, and nine aluminums have been structurally characterized. Aluminox-

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(1) Kaminsky, W.; Sinn, H. *Proc. IUPAC, IUPAC, Macromol. Symp.* **1982**, 28, 247.

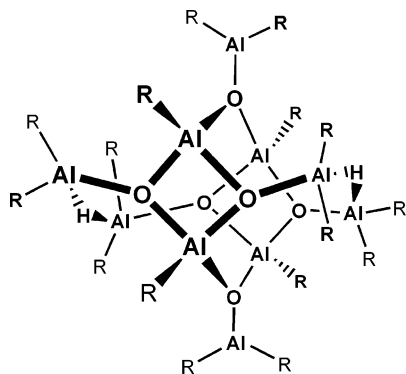
(2) Chen, E. Y.-X.; Marks, T. J. *Chem. Rev. (Washington, DC, U.S.)* **2000**, 100 (4), 1391–1434.

(3) Storr, A.; Jones, K.; Laubengayer, A. W. *J. Am. Chem. Soc.* **1968**, 90 (12), 3173–7.

(4) Giannini, U.; Albizzati, E.; Zucchini, U. *Inorg. Chim. Acta* **1985**, 98 (3), 191–4.

(5) Mason, M. R.; Smith, J. M.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1993**, 115 (12), 4971–84.

(6) Harlan, C. J.; Mason, M. R.; Barron, A. R. *Organometallics* **1994**, 13 (8), 2957–69.

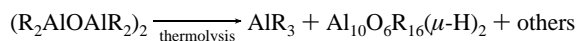
Scheme 1. $\text{Al}_{10}\text{O}_6\text{Bu}_{16}(\mu\text{-H})_2$, R = $i\text{Bu}$ 

anes with ring and ladder structures have been synthesized starting from $(\text{Mes}^*\text{AlH}_2)_2$, where Mes^* is 2,4,6-tri-*tert*-butylbenzene.⁷ Controlled thermolysis of anionic methylaluminoxanes has yielded a large, open anionic cluster.⁸

During studies of hydrolyzed isobutylaluminoxane, as the MAO replacement, we serendipitously obtained nice single crystals of $\text{Al}_{10}\text{O}_6\text{Bu}_{16}(\mu\text{-H})_2$ (**I**, Scheme 1). This material is extremely useful for NMR characterization and molecular orbital calculation assessment as a model for methylaluminoxanes.

Experimental Section

Single crystals of $\text{Al}_{10}\text{O}_6\text{Bu}_{16}(\mu\text{-H})_2$ (**I**, Scheme 1) were obtained from long-term storage (>6 months at ambient temperature) of neat $(i\text{Bu}_2\text{AlOAl}^i\text{Bu}_2)_2$ obtained by hydrolyzing triisobutylaluminum with 0.5 equiv of water; several attempts to make compound **I** starting from $i\text{Bu}_2\text{AlH}$ failed. The formation of the crystals from neat $(i\text{Bu}_2\text{AlOAl}^i\text{Bu}_2)_2$ is a very slow process at room temperature, and the yield is low (<0.1% after one year). Subsequently, we found that the reaction can be accelerated by heating neat $(i\text{Bu}_2\text{AlOAl}^i\text{Bu}_2)_2$ at $\sim 80^\circ\text{C}$ for 6–8 h, during which a disproportionation reaction occurs generating Al^iBu_3 , **I**, and a number of hydride-containing species:



The reaction can be conveniently monitored by ^1H NMR for the formation of Al^iBu_3 and the hydride. The thermolysis, if done at 60°C or $>110^\circ\text{C}$, results in either too slow a reaction or the formation of a black Al metal, respectively. After removal of Al^iBu_3 from the mother liquor ($80^\circ\text{C}/0.3\text{ mmHg}$), the yield of **I** can reach up to $\sim 10\%$.

The crystal of $\text{Al}_{10}\text{O}_6\text{Bu}_{16}(\mu\text{-H})_2$ is triclinic (space group $P\bar{1}$) and contains both near-linear bridging hydrides ($\angle\text{Al4-H-Al5} = 154(2)^\circ$, $d(\text{Al-H}) = 1.72(3)\text{ \AA}$) and nearly planar three-coordinate aluminum sites ($\angle\text{C9-Al3-C13} = 134.6(1)^\circ$; Al3 is 0.0304(6) Å out of the C9–C13–O3 plane).

NMR studies of this air-sensitive compound were done at the National High Magnetic Field Laboratory on a narrow-bore Magnex 19.6 T (833 MHz, ^1H) magnet fitted with a Bruker console and a Samoson probe. NMR spectra were also acquired on the hybrid 40 T magnet with a Tecmag console and the Samoson probe. Magnetic

(7) Wehmschulte, R. J.; Power, P. P. *J. Am. Chem. Soc.* **1997**, *119* (35), 8387–8388.

(8) Atwood, J. L.; Hrcir, D. C.; Priester, R. D.; Rogers, R. D. *Organometallics* **1983**, *2* (8), 985–9.

Table 1. Calculated and Experimental ^{27}Al NMR Parameters

site	calculated				experimental		
	charge/e ⁻	C_q/MHz	η	δ/ppm^a	C_q/MHz	η	δ/ppm^a
Al1, AlCO_3	0.446	-17.3	0.319	113	17.5	0.41	117
Al3, AlC_2O	0.572	37.2	0.731	211			
Al4, $\text{AlC}_2\text{O}(\mu\text{-H})$	0.336	-20.9	0.663	149	22.9	0.67	158

^a Experimental chemical shifts are referenced to the $\text{Al}(\text{NO}_3)_3$ solution (0 ppm); calculated chemical shifts are referenced to the trimethylaluminum dimer with 5-coordinate bridging carbons (154 ppm).

fields were calibrated with $\alpha\text{-Al}_2\text{O}_3$ (-8.8 ppm).⁹ Magic-angle spinning (MAS) rotors, 2.0 mm ZrO_2 rotors with tight-fitting Kel-F caps, were loaded in an argon-filled glovebox and transported to the NMR instrument in capped vials and spun with air to 35.7 kHz for up to 40 min. Under these conditions, the more air-sensitive MAO samples gave spectra without noticeable decomposition products and three different samples of **I** gave very similar spectra. Despite the field calibration with $\alpha\text{-Al}_2\text{O}_3$, the 40 T field was observed to drift between sample changes; hence, the chemical shifts reported here are based on the 19.6 T spectra. Alternative data acquisition strategies, such as an internal chemical shift standard, were considered, but none were found; AlB_2 was considered as it has a chemical shift well away from **I**, but the AlB_2 resonance has a broad intrinsic line width.¹⁰ Other experimental details for 40 T NMR spectroscopy are reported elsewhere.¹¹

The three-coordinate site was not included in the fit because the calculated C_q (37.2 MHz; Table 1) is much too large to yield a detectable resonance at 19.6 or 40 T and at a 35 kHz spin rate.⁹ The experimental ^{27}Al C_q , η , and isotropic chemical shift values are given in Table 1. The four-coordinate aluminum sites have, as expected, similar chemical shifts, while the three-coordinate site is believed to be shifted as much as 100 ppm downfield.¹² In an effort to extract the maximum information from the 19.6 and 40 T spectra, a spectral fitting procedure was designed to simultaneously fit all spectra, using a Nelder–Mead Simplex algorithm¹³ provided in Matlab. **I** has quite high symmetry as it lies on an inversion center; hence, the 10 aluminum sites in the molecule reduce to three NMR distinct sites in the MAS spectra. The four sites labeled “ AlCO_3 ” (see Scheme 1) contribute to one ^{27}Al resonance, and the four sites labeled “ $\text{AlC}_2\text{O}(\mu\text{-H})$ ” contribute to another; the two sites labeled “ AlC_2O ” have C_q values too large to be observed, even at 40 T.⁹ (The *tert*-butyl analogue of the dimer $(\text{R}_2\text{AlOAlR}_2)_2$ has been structurally characterized by single-crystal X-ray determination. In contrast, the isobutyl analogue is a liquid at room temperature. See refs 5, 6, and 24.)

Results and Discussion

The ^1H NMR spectrum of the crystals, having an empirical formula of $\text{Al}_{10}\text{O}_6\text{Bu}_{16}\text{H}_2$ (**I**), exhibits characteristics very different from those of $(\text{R}_2\text{AlOAlR}_2)_2$, namely, four different alkyl environments (in a 1:1:1:1 ratio), very sharp resonances (indicative of slow or no alkyl exchange), and the presence

(9) Bryant, P. L.; Harwell, C. R.; Mrse, A. A.; Emery, E. F.; Gan, Z.; Caldwell, T.; Reyes, A. P.; Kuhns, P.; Hoyt, D. W.; Simeral, L. S.; Hall, R. W.; Butler, L. G. *J. Am. Chem. Soc.* **2001**, *123* (48), 12009–12017.

(10) Eastman, M. A. *J. Magn. Reson.* **1999**, *139* (1), 98–108.

(11) Gan, Z. H.; Gor'kov, P.; Cross, T. A.; Samoson, A.; Massiot, D. *J. Am. Chem. Soc.* **2002**, *124* (20), 5634–5635.

(12) Benn, R.; Janssen, E.; Lehmkühl, H.; Rufinska, A. *J. Organomet. Chem.* **1987**, *333* (2), 155–168.

(13) Lagarias, J. C.; Reeds, J. A.; Wright, M. H.; Wright, P. E. *SIAM J. Optim.* **1998**, *9* (1), 112–147.

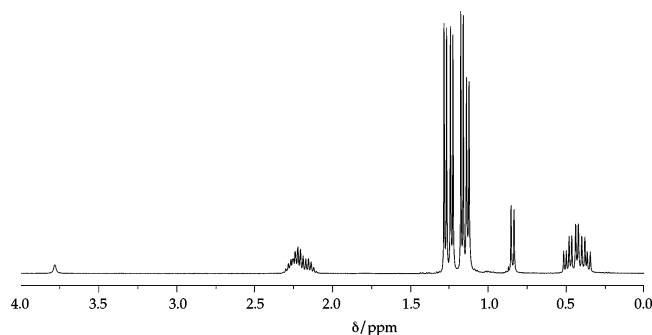


Figure 1. ^1H NMR spectrum of **I**.

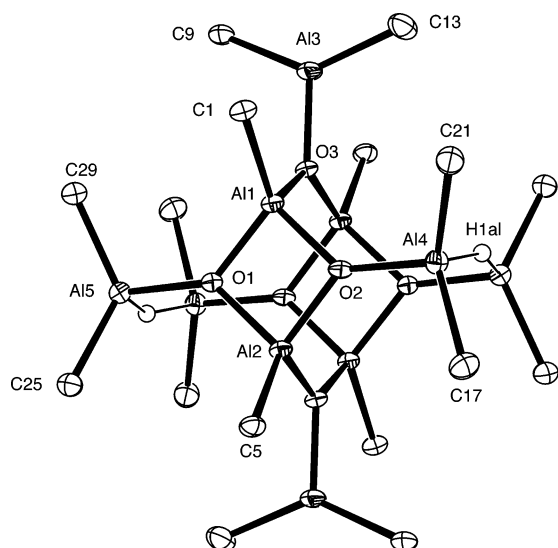


Figure 2. ORTEP of the core of the cluster, $\text{Al}_{10}\text{O}_6\text{Bu}_{16}(\mu\text{-H})_2$, **I**. For each isobutyl group, only one carbon is shown. With a molecular symmetry of C_{2h} , the unique sites are as follows: Al1, a four-coordinate AlCO_3 site; Al3, a three-coordinate AlC_2O site; and Al4, a four-coordinate $\text{AlC}_2\text{O}(\mu\text{-H})$ site.

of a broad hydride resonance at 3.80 ppm (Figure 1). The presence of a hydride (8:1 isobutyl/hydride ratio) is unexpected, but not surprising considering the ease with which an isobutyl group can undergo $\beta\text{-H}$ elimination.

This complex (Figure 2) is the first aluminoxane found to contain a bridging hydride. Among related alkyl systems, trimeric di-*tert*-butylaluminum hydride has a slightly bent bridging hydride with $d(\text{Al}-\text{H}) = 1.726(5)$ Å and $\angle\text{Al}-\text{H}-\text{Al} = 151(1)^\circ$.¹⁴ The anionic alane, $\text{Na}[(\text{CH}_3)_3\text{Al}-\text{H}-\text{Al}(\text{CH}_3)_3]$ has a linear bridging hydride with $d(\text{Al}-\text{H}) = 1.665(1)$ Å.¹⁵ A bridging hydride, $d(\text{Al}-\text{H}) = 1.803(7)$ and $1.829(8)$ Å, is found in the benzoate complex, $\text{R}_2\text{Al}(\mu\text{-H})(\mu\text{-O}_2\text{C}-\text{C}_6\text{H}_5)\text{AlR}_2$ ($\text{R} = \text{CH}(\text{SiMe}_3)_2$).¹⁶ A similar bond length, $1.727(1)$ Å, is found in a doubly bridging hydride, bis(bis(trimethylsilyl)amino)alane dihydride, $\{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\mu\text{-H})_2\}_2$.¹⁷

Aluminoxanes have been difficult to study with ^{27}Al MAS NMR because of very large ^{27}Al quadrupolar interactions

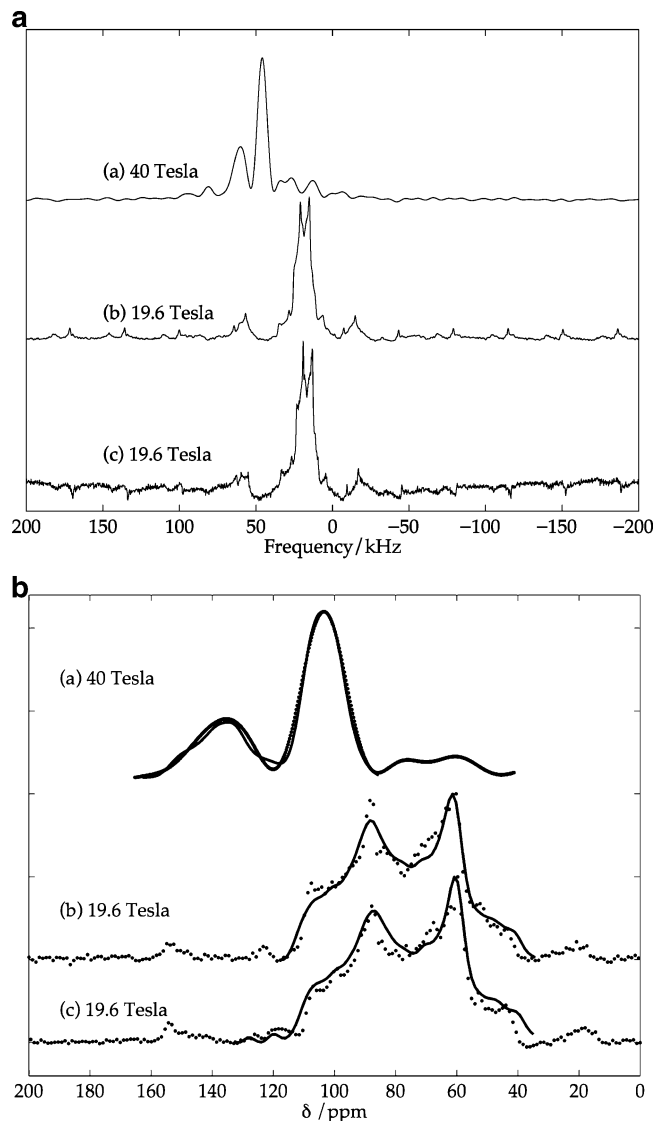


Figure 3. (a) ^{27}Al MAS NMR spectrum at $B_0 = 19.6$ T, $\nu_r = 35.7$ kHz (two runs) and $B_0 = 40$ T, $\nu_r = 35$ kHz. (b) Best Simplex fits of the central transition of the ^{27}Al MAS NMR spectrum.

which yield extremely broad resonances, even at high magnetic fields and fast MAS rates.⁹ In advance of the NMR studies of **I** (Figure 3), ab initio molecular orbital calculations were performed for an idealized structure; isobutyl groups were replaced by methyl groups and the molecular symmetry was increased from C_{2h} to D_{2h} . Previous calculations have demonstrated that the Hartree–Fock-level calculations are sufficient to obtain C_q and η values within 10% of experimental solid-state NMR parameters.⁹ The ab initio restricted Hartree–Fock calculations, with a double- ζ basis set (cc-pVDZ), yielded an optimized geometry for which Löwdin charges,¹⁸ ^{27}Al quadrupolar NMR parameters, C_q , and η were calculated (Table 1).

In the MAO/metalocene polyolefin catalysis, three-coordinate aluminum sites in MAO were originally thought necessary for catalytic activation of the metallocenes. It was proposed that the Lewis acidity of a three-coordinate aluminum site would enable the extraction of a ligand from

(14) Uhl, W. *Z. Anorg. Allg. Chem.* **1989**, *570*, 37–53.

(15) Atwood, J. L.; Hrnčir, D. C.; Rogers, R. D.; Howard, J. A. K. *J. Am. Chem. Soc.* **1981**, *103* (22), 6787–8.

(16) Uhl, W.; Graupner, R.; Pohl, S.; Saak, W.; Hiller, W.; Neumayer, M. *Z. Anorg. Allg. Chem.* **1997**, *623* (5), 883–891.

(17) Janik, J. F.; Wells, R. L.; Rheingold, A. L.; Guzei, I. A. *Polyhedron* **1998**, *17* (23–24), 4101–4108.

(18) Löwdin, P.-O. *Phys. Rev.* **1955**, *97*, 1474–89.

the metallocene, thus opening a coordination site for an olefin.^{1,2,19} However, that concept has evolved into a more sophisticated mechanism of "latent Lewis acidity"¹⁹ in which four-coordinate aluminum sites have, because of strain within cage complexes, the potential to rupture and thus generate reactive three-coordinate sites. Another scheme by which three-coordinate aluminum sites might be generated is the cleavage of a bridging methyl bond. Recently, bridging methyls have been observed in MAO by Fourier transform infrared (FTIR) spectroscopy²⁰ and it was reported that the *tert*-butylaluminum hexamer reacts with trimethylaluminum to form methyl bridges, and this product is catalytically active with metallocenes.²¹ Well-defined three-coordinate aluminum sites are rare, with the sterically hindered, non-catalytically active site of $Al(OR)_3$ ($R = 2,6$ -di-*tert*-butyl-4-methylphenyl) available as one example.²² Preliminary testing shows that **I** has little or no activating power for a number of metallocenes tested. Typically, the 1H NMR spectrum of Cp_2ZrMe_2 in C_6D_6 remains unchanged after mixing with 1 equiv of **I**. This lack of reactivity is apparently due to the bulky isobutyl groups protecting the three-coordinate aluminum (Al_3).

Despite the lack of catalytic activity, the title compound is highly important to MAO structural research for several reasons: a well-characterized three-coordinate aluminum site and a bridging hydride site, a large aluminum cluster size, a total of 10 aluminum sites, and an empirical formula ($Al_{1.0}O_{0.6}R_{1.6}$) which is similar to that determined for MAO ($Al_{1.0}O_{0.8-0.75}R_{1.4-1.5}$).²³ The lack of catalytic activity is attributed to the bulk isobutyl groups which prevent the three-coordinate aluminum sites from extracting a methyl from dimethyl zirconocene and adopting a tetrahedral geometry.

A search for three-coordinate sites in MAO was made with field-swept NMR with the assumption that ^{27}Al $C_q > 30$ MHz, but no such sites were found.⁹ In the present work, the calculated $C_q = 37.2$ MHz and, based on the accuracy for the two other sites, we estimate an accuracy of ± 3 MHz. With such a large C_q and after reconsidering the earlier field-swept spectra, the three-coordinate sites may not have been detected if they were present in less than 10% abundance. The charge distribution among the aluminum sites shows that the three-coordinate sites have the highest positive charge, consistent with their proposed role as Lewis acids. The hydride site creates the potential for a facile change in the aluminum charge upon rupture of an $Al-H-Al$ bond for one of the aluminum sites, from least positive to most positive. Because of the crystalline form of this aluminosane, it has unique value in the calculations and NMR spectroscopy of MAO, especially with the validation of the calculated quadrupolar interactions and chemical shifts.

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Supporting Information Available: Crystallographic data, including the coordinates of the idealized structure used for the calculations (9 pages). This material is available free of charge via the Internet at <http://pubs.acs.org>

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- (19) Harlan, C. J.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1995**, *117* (24), 6465–74.
 (20) Ystenes, M.; Eilertsen, J. L.; Liu, J.; Ott, M.; Rytter, E.; Støvneng, J. A. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38* (17), 3106–27.
 (21) Watanabe, M.; McMahon, C. N.; Harlan, C. J.; Barron, A. R. *Organometallics* **2001**, *20* (3), 460–467.
 (22) Healy, M. D.; Barron, A. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31* (7), 921–2.

- (23) Imhoff, D. W.; Simeral, L. S.; Blevins, D. R.; Beard, W. R. *ACS Symp. Ser.* **2000**, *749*, 177–191.
 (24) Boleslawski, M.; Serwatowski, J. *J. Organomet. Chem.* **1983**, *254* (2), 159–66.