Synthesis and Molecular Structure of $(^tBuOO)(^tBuO)Al(\mu\text{-}O^tBu)_2Al(mesal)_2$. The First Structurally Characterized (Alkylperoxo)aluminum Compound

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Organoaluminum compounds are usually very sensitive toward dioxygen and very often inflame spontaneously in the air. Mild oxidation of these compounds by controlled introduction of oxygen leads to alkoxide compounds via unstable alkyl peroxide intermediates.[1] Although the reactions of a variety of aluminum trialkyls with dioxygen and organic peroxides have been under investigation for many years,[2] no structural data are available for aluminum alkyl peroxide. Only recently the first stable alkyl peroxide compounds of group 13 have been isolated and structurally characterized (e.g. $[(^tBu)_2M(\mu\text{-}OO^tBu)]_2$; M = Ga, In)[3,4] from the reaction of tri(*tert*-butyl) derivatives with dioxygen. A similar reaction of $Al(^tBu)_3$ with dioxygen results in the formation of the corresponding monoalkoxide compound $[(^tBu)_2Al(\mu\text{-}O^tBu)]_2$).[5] We report here the isolation and structural characterization of the first (alkylperoxo)aluminum compound derived from the oxidation of di-*tert*-butylaluminum O,O′-chelate complex.

The *tert*-butyl substituted dialkylaluminum chelate compound was obtained from the equimolar reaction of $(^tBu)_3Al{\cdot}OEt_2$ and methyl salicylate (mesalH) in a near quantitative yield (eq 1).[6]

$$(^tBu)_3Al{\cdot}OEt_2 + \text{mesalH} \rightarrow (^tBu)_2Al(\text{mesal}) + {}^iBuH \qquad (1)$$

The interaction of $(^tBu)_2Al(mesal)$ (**1**) with dry dioxygen at −15 °C leads to the formation of $(^tBuOO)(^tBuO)Al(\mu\text{-}O^tBu)_2Al(mesal)_2$ (**2**) in an essentially quantitative yield (eq 2).[7]

In contrast to the results observed for $(^tBu)_3Al$, where only one alkyl group reacts with dioxygen,[8] reaction 2 proceeds with oxidation of both ^tBu groups in the four-coordinated $(^tBu)_2Al(mesal)$ (**1**) chelate complex. Compound **2** is stable as a solid under an air atmosphere at ambient conditions but slowly decomposes in solution. The same reaction carried out at room temperature results in the formation of a complex mixture of products difficult to identify.

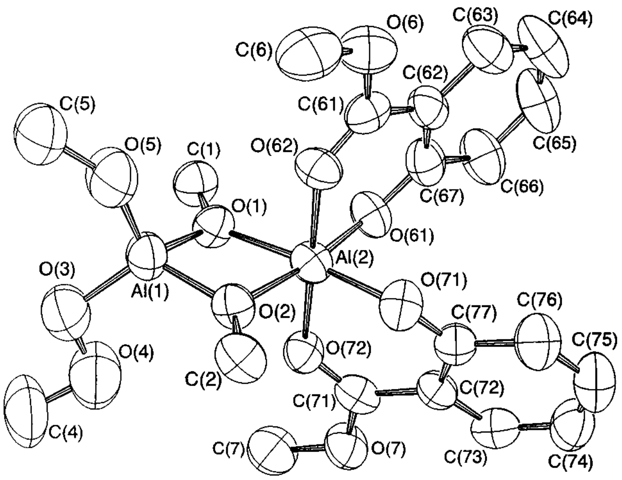
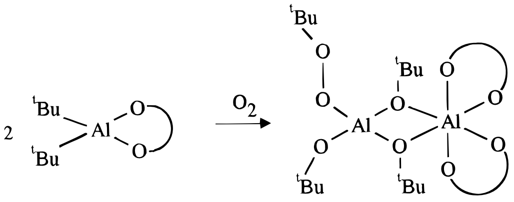


Figure 1. Molecular structure of $(^tBuOO)(^tBuO)Al(\mu\text{-}O^tBu)_2Al(mesal)_2$ (**2**). Thermal ellipsoids are drawn at the 50% level. All hydrogen atoms and methyl groups of the *tert*-butyl substituents are omitted for clarity.



(2)

(**1**) (**2**)

The solid state structure of **2** has been confirmed by X-ray crystallography[8] and is essentially consistent with spectroscopic data.[7] The molecular structure of **2** is shown in Figure 1. The molecule has an unsymmetric dinuclear structure with two aluminum atoms of different coordination. The Al(1) atom is bonded to a *tert*-butyl peroxide group and one terminal *tert*-butoxide group and Al(2) to two chelating mesal ligands. Both aluminum sites are joined by bridging μ_2-*tert*-butoxide groups. The *tert*-butyl peroxide group is terminally bonded by the O(3) atom with a Al(1)−O(3) distance of 1.725(7) Å. The peroxo O(3)−O(4) bond distance of 1.38(2) Å is slightly shorter in comparison to those found for other monodentate and bridging alkyl peroxides coordinated to main group[3,4,9] and transition metals.[10] The second oxygen atom O(4) of the alkylperoxo moieties is situated in a distance of 2.50(2) Å from the Al(1) atom. The Al(1)−O(4) distance must be considered as quite long and is outside the normal range observed for Al−O bonds

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[1] For reviews, see: (a) Brilkina, T. G.; Shushunov, V. A. *Reaction of Organometallic Compounds with Oxygen and Peroxides*; Nauka: Moscow, 1966; p 226. (b) Alexandrov, Y. A.; Chikinova, N. V. *J. Organomet. Chem.* **1991**, *418*, 1.

[2] For earliest work, see, for example: (a) Razuvaev, G. A.; Mitrofan, E. V.; Petukhov, G. G.; *Zh. Obshch. Khim.* **1961**, *31*, 2343. (b) Razuvaev, G. A.; Graevskii, A. I. *Zh. Obshch. Khim.* **1962**, *32*, 1006. (c) Razuvaev, G. A.; Graevskii, A. I.; Minsker, K. S.; Zakharova, V. N. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* **1962**, 1555.

[3] Cleaver, W. M.; Barron, A. R. *J. Am. Chem. Soc.* **1989**, *111*, 8966.

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

[5] Barron, A. R. *Chem. Soc. Reviews*, **1993**, 93.

[6] To a solution of $^tBu_3AlOEt_2$ (4 mmol) in hexane (15 cm^3), methyl salicylate (4 mmol) was slowly added at 0 °C. The solution was warmed up to room temperature in 0.5 h. The solvent was evaporated in vacuo at ambient temperature. The resulting white product was recrystallized from toluene/hexane solution. ^1H NMR (δ ppm, C_6D_6): 1.27 (s, 18H, $Al{-}^tBu$), 3.05 (s, 3H, OCH_3), 6.34 (td, 1H, Ar−H), 6.92 (dd, 1H, Ar−H), 7.02 (td, 1H, Ar−H), 7.47 (dd, 1H, Ar−H).

[7] A solution of $(^tBu)_2Al(mesal)$ (0.8 g, 2.6 mmol) in toluene (7 cm^3) was cooled to −15 °C and then was exposed to the action of dry atmospheric oxygen ($CaCl_2$ was placed at the inlet of the Schlenk flask to present the access of moisture). The oxidation was carried out for 2 h. The solvent was removed under vacuum, yielding a white crystalline solid. Anal. Calcd (Found) for $C_{32}H_{50}Al_2O_{11}$: C, 57.82 (57.91); H, 7.58 (7.74). ^1H NMR (δ ppm, C_6D_6): 1.38 (s, 9H, ^tBuO), 1.49 (s, 9H, ^tBuO), 1.60 (s, 9H, ^tBuO), 1.61 (s, 9H, ^tBuO), 3.77 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 6.38 (t, 2H, Ar−H), 6.57 (t, 2H, Ar−H), 6.92 (t, 2H, Ar−H), 7.79 (d, 2H, Ar−H).

[8] $(^tBuOO)(^tBuO)Al(\mu\text{-}O^tBu)_2Al(mesal)_2$ crystallizes in an orthorhombic crystal system, *Pbca* space group, $T = 20$ °C, $a = 15.171(3)$ Å, $b = 18.542(6)$ Å, $c = 26.827(7)$ Å, $Z = 8$. 4659 reflections and 140 restraints were used for refinement of 464 parameters against F^2, goodness of fit 1.061, conventional $R_1 = 0.0698$ for 2136 data with $I > 2\sigma(I)$, $wR_2 = 0.1454$ for all data. The peroxide and alkoxide ligands were disordered over two opposite sites, almost mirrored against a plane defined by the central Al_2O_2 ring. The disorder was modeled in terms of two sets of $Al(O^tBu)(OO^tBu)$ atoms with refined occupancy factors 0.75(1) and 0.25(1). The group showing SOF = 0.25(1) was refined isotropically with geometrical restraints assuming that chemically equivalent distances in both groups were nearly equal.

[9] (a) Starikova, Z. A.; Shchegoleva, T. M.; Trunov, V. K.; Pokrovskaya, I. E.; Kanunnikova, E. N. *Kristallografiya* **1979**, *24*, 1211. (b) Shklover, V. E.; Struchkov, Yu. T.; Dodonov, V. A.; Zinov'eva, T. I.; Antonovskii, V. L. *Metalloorg. Khim. (Organomet. Chem. in USSR)* **1988**, *1*, 1140. (c) Starikova, Z. A.; Shchegoleva, T. M.; Trunov, V. K.; Pokrovskaya, I. E. *Kristallografiya* **1978**, *23*, 969. (d) Balch, A. L.; Cornman, C. R.; Olmstead, M. M. *J. Am. Chem. Soc.* **1990**, *112*, 2963.

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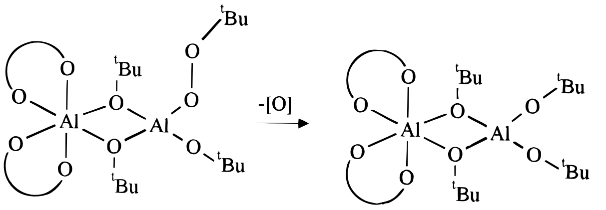
(one of the longest Al−O distances is found for a five-coordinated cation $[AlMe_2{\cdot}[18]crown\text{-}6]^+$, 2.435(5) Å[11]). Another notable feature concerning the *tert*-butylperoxo ligand is the almost planar geometry of the AlOOC unit with a torsion angle of 176(1)°, in contrast to the geometry observed for other nonbridging alkyl peroxides bonded to the main group metals (Sb and Ge) where the M−O−O−C torsion angles are in the range from 121.7° to 147.4°.[9] In addition, the Al(1)−O(3)−O(4) and O(3)−O(4)−C(4) angles (106.9(7)° and 101(1)°, respectively) are comparable to the corresponding values in the reported monodentate alkyl peroxides.[9,10] Structurally characterized gallium and indium alkyl peroxides described recently contained bridging alkylperoxo groups,[3,4] and in one case the spectroscopic characterization of a terminal alkyl peroxide of gallium was reported.[12] Compound **2** represents the first structurally characterized terminal alkyl peroxide for a heavier group 13 element.

The coordination geometry of Al(1) is pseudotetrahedral with the smallest O(1)−Al(1)−O(2) angle being 83.3(2)°, associated with strains in the central $Al_2(\mu\text{-}O)_2$ ring. The Al(1)−O(5) bond distance, 1.69(1) Å, is typical for a terminal aluminum−alkoxide bond (cf., the Al−O terminal distances in the dimer $[({}^tBuO)_2Al(\mu\text{-}O{}^tBu)]_2$[13] and $[Al(OSiMe_3)_2(acac)]_2$[14] are 1.69 and 1.70 Å, respectively). The $Al_2(\mu\text{-}O)_2$ bridges are asymmetric with the longer bond being to the six-coordinate aluminum, and the Al−O distances are similar to that of the aluminum dialkoxide chelate complex.[14] The Al(2)−O(62) and Al(2)−O(72) distances of 1.925(4) and 1.922(4) Å, respectively, are comparable with related bond distances in the monomeric five-coordinate complex $MeAl(mesal)_2$.[15] The coordination geometry of Al(2) is almost ideal octahedral with the small deviation being the O(1)−Al(2)−O(2) angle of 76.3(2)° imposed by the strains in the central $Al_2(\mu\text{-}O)_2$ ring. Surprisingly, overall the structure of compound **2** is similar to that of aluminum dialkoxide chelate complexes $[Al(OR)_2(\beta\text{-diketonate})]_2$,[14] whereas the latter have been obtained in the redistribution reaction of $(RO)_3Al$ and corresponding $Al(\beta\text{-diketonate})_3$.

The ^1H NMR spectrum of **2** is essentially consistent with the structure found in the solid state. In the spectrum two singlets of $-OCH_3$ protons of chelating mesal ligands are observed, as well as four singlets of $-C(CH_3)_3$ protons corresponding to one ${}^tBuOO$ group and three ${}^tBuO$ groups with different environments. The bridging alkoxides have different environments because there is no mirror plane in the molecule (both aluminum atoms are chiral). The environment of *tert*-butyl C(1) is such that the alkoxide group and the *facial* mesal ligand are on the same side of the Al_2O_2 ring. In contrast, *tert*-butyl C(2) has the peroxide and the *facial* mesal ligand on the same side of the Al_2O_2 ring.

$({}^tBuOO)({}^tBuO)Al(\mu\text{-}O{}^tBu)_2Al(mesal)_2$ shows slow decomposition in solution at room temperature, and in a period of several hours the ^1H NMR resonances of the peroxide compound **2** decay while new resonances appear in the spectrum. We assume that these latter resonances arise from the decomposition of the *tert*-butyl peroxide ligand to the *tert*-butyl peroxide group with formation of aluminum dialkoxide chelate complexes $({}^tBuO)_2Al(\mu\text{-}O{}^tBu)_2Al(mesal)_2$ (**3**) (eq 3).



(3)

(**2**) (**3**)

Studies on the interation of dialkylaluminum chelate complexes with dioxygen and the stability and reactivity of alkyl peroxide aluminum compounds are underway in our laboratory.

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Supporting Information Available: A listing of crystallographic data, atomic parameters, anisotropic thermal parameters, and complete bond distances and angles for **2** (8 pages). See any current masthead page for ordering and Internet access instructions.

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