

## A Hydrogen Bonded Aluminium Alkoxide Hydroxide Aggregate Resulting from the Exposure of Methylaluminium Dichloride to Air

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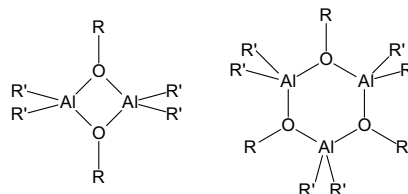
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Exposure of methylaluminium dichloride to air results in the formation of a crystalline hydrolysis/oxidation product of the composition  $[(\text{MeOAlCl}_2)_3][(\text{MeOAlCl}_2)_2(\text{HOAlCl}_2)]$ , which is linked by a  $\text{H}\cdots\text{Cl}$  hydrogen bond in the solid state. Oxygen is thus inserted into the carbon-aluminium bond in the primary reaction, whereas hydrolysis plays only a minor role.

**Key words:** Aluminium, Alkoxides, Aggregation

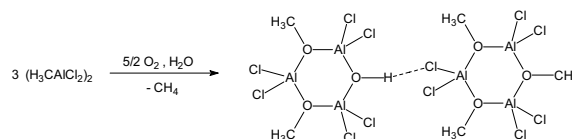
Due to the practical and technical importance of aluminium alkyls, their behaviour towards the components of air is of fundamental interest. The interaction with dioxygen has been studied quite extensively over a period of several decades [1]. In a recent contribution to this field Lewiński and co-workers reported the insertion of oxygen into Al–C bonds resulting in alkoxide aggregates, but also alkylperoxide complexes, which contain  $\eta^2$ -terminally bonded *t*BuOO groups at aluminium [2]. The reactions with aluminium alkyls with the humidity of air are also of great technical significance due to the use of alumoxanes as active co-catalysts in olefin polymerisation [3]. The reactions of organometallic group 13 compounds with water and the resulting molecular structures were recently reviewed by Roesky and coworkers [4]. Since the first structural characterisation of alkyl-alumoxanes [5] a variety of structural motifs of Al/O aggregates was found including those with bridging OH groups in alumoxane aggregates [6].

The two most frequently observed types of aggregation are shown in Scheme 1, exhibiting  $\text{Al}_2\text{O}_2$  four-membered rings and  $\text{Al}_3\text{O}_3$  six-membered rings.



Scheme 1.

In this contribution we report on the formation of a mixed alkoxide/hydroxide aggregate, which results from exposing methylaluminium dichloride solutions in hexanes to air. Under these conditions oxidative insertion of oxygen atoms into the aluminium-carbon bonds and hydrolysis of Al-bound methyl groups occurs simultaneously, as was observed in the crystalline reaction product  $[(\text{MeOAlCl}_2)_3][(\text{MeOAlCl}_2)_2(\text{HOAlCl}_2)]$ , identified by elemental analysis and a determination of its crystal structure (see below). The hydrolysis of the Al–Cl functions seems not to be a preferred reaction pathway. The overall reaction can be summarised as follows.



Scheme 2.

The triclinic crystals (space group  $P\bar{1}$ ) contain two different aluminium alkoxide rings, one with one hydroxyl and two methoxy groups,  $[(\text{MeOAlCl}_2)_2(\text{HOAlCl}_2)]$ , and one with three methoxy groups,  $[(\text{MeOAlCl}_2)_3]$ . A plot of the structure is provided in Fig. 1, a selection of structural parameters given in Table 1. The two ring units are linked through a hydrogen bond between the OH proton of  $[(\text{MeOAlCl}_2)_2(\text{HOAlCl}_2)]$  and a chlorine atom of  $[(\text{MeOAlCl}_2)_3]$ . Pure  $[(\text{MeOAlCl}_2)_3]$  has been described previously [7] and was prepared by reacting a solution of methylaluminium dichloride in hexanes with methanol.

In the aggregate  $[(\text{MeOAlCl}_2)_3][(\text{MeOAlCl}_2)_2(\text{HOAlCl}_2)]$  two of the three shortest Al–O bonds are those to the hydroxy group (1.793(1) and 1.794(1) Å), while only one of the Al–O bonds to a methoxy group is even shorter (1.788(1) Å). The other five bond lengths of this type are between 1.795(1) and 1.811(1) Å.

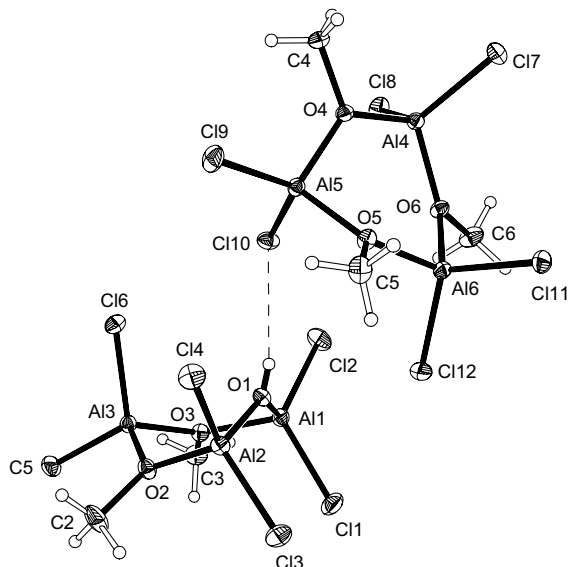


Fig. 1. Molecular structure of  $[(\text{MeOAlCl}_2)_3] \cdot [(\text{MeOAlCl}_2)_2(\text{HOAlCl}_2)]$  as determined by low-temperature X-ray crystallography.

Table 1. Selected structural parameter values for  $[(\text{MeOAlCl}_2)_3][(\text{MeOAlCl}_2)_2(\text{HOAlCl}_2)]$ .

Bond lengths [Å]		Bond angles [°]	
O1–Al1	1.793(1)	Al1–O1–Al2	132.2(1)
O1–Al2	1.794(1)	Al2–O2–Al3	122.3(1)
O2–Al2	1.803(1)	Al1–O3–Al3	123.6(1)
O2–Al3	1.811(1)	Al5–O4–Al4	124.1(1)
O3–Al1	1.797(1)	Al6–O6–Al4	133.3(1)
O3–Al3	1.799(1)	Al6–O5–Al5	124.0(1)
O4–Al5	1.788(1)	O1–Al1–O3	96.8(1)
O4–Al4	1.795(1)	O1–Al2–O2	96.0(1)
O5–Al6	1.795(1)	O3–Al3–O2	103.4(1)
O5–Al5	1.795(1)	O4–Al5–O5	101.2(1)
O6–Al6	1.800(1)	O4–Al4–O6	101.2(1)
O6–Al4	1.803(1)	O5–Al6–O6	100.6(1)
O1–H1	0.68(3)	O1–Al1–Cl2	109.8(1)
Al1–Cl2	2.085(1)	O3–Al1–Cl2	112.6(1)
Al1–Cl1	2.093(1)	O1–Al1–Cl1	110.8(1)
Al2–Cl3	2.084(1)	O3–Al1–Cl1	108.0(1)
Al2–Cl4	2.094(1)	Cl2–Al1–Cl1	117.0(1)
Al3–Cl5	2.092(1)	Al1–O1–H1	113(3)
Al3–Cl6	2.100(1)	Al2–O1–H1	115(3)
Al4–Cl8	2.093(1)	Al2–O2–C2	116.3(1)
Al4–Cl7	2.094(1)	Al3–O2–C2	120.3(1)
Al5–Cl9	2.075(1)		
Al5–Cl10	2.117(1)		
Al6–Cl12	2.087(1)		
Al6–Cl11	2.102(1)		
O2–C2	1.470(2)		
O3–C3	1.473(2)		
O4–C4	1.476(2)		
O5–C5	1.479(2)		
O6–C6	1.485(2)		

Both  $\text{Al}_3\text{O}_3$  rings can be described to adopt approximately a boat conformation. The Al–O–Al angles are relatively wide. In each ring there is one Al–O–Al angle, which is much larger than the other two causing pronounced asymmetry in the aggregates. The  $[(\text{MeOAlCl}_2)_2(\text{HOAlCl}_2)]$  ring contains two smaller Al–O–Al angles ( $122.3(1)^\circ$  and  $123.6(1)^\circ$ ) involving the methoxy groups and a larger one of  $132.2(1)^\circ$  at the hydroxy oxygen atom. This is, however, not a phenomenon inherently related to the OH group, because in  $[(\text{MeOAlCl}_2)_3]$  the ring also has two smaller angles with  $124.0(1)^\circ$  and a larger one at  $133.3(1)^\circ$  (Al4–O6–Al6), and this involves a methoxy group. This result is clearly at variance with the reported structure of  $(\text{MeOAlCl}_2)_3$ , which has three similar Al–O–Al angles ( $121.9$ ,  $122.4$  and  $122.8^\circ$ ) [7] and shows how flexible such ring geometries with a large ionic contribution to bonding are. Notwithstanding, the conformation of both  $[(\text{MeOAlCl}_2)_3]$  rings in lit. [7] and in the present study is quite similar.

All oxygen atoms of the methoxy groups have planar coordination geometries as is indicated by the sum of angles about these atoms which are between  $359.4$  and  $360.0^\circ$ . The coordination geometry at the oxygen atom of the hydroxy group is also planar (sum of angles  $360^\circ$ ). In context with the wide Al–O–Al angles this requires the C–O–Al angles to be smaller than the latter. For all methoxy oxygen atoms but O6 there is one slightly smaller angle ( $116.3$ ,  $114.8$ ,  $114.7$ ,  $115.4^\circ$ ) and a larger one ( $120.3$ ,  $121.5$ ,  $120.7$ ,  $120.1^\circ$ ). The oxygen atoms involved in large Al–O–Al angles (see above) have smaller C–O–Al (O6:  $112.1$  and  $114.1^\circ$ ) or H–O–Al angles (O1:  $113$ ,  $115^\circ$ ).

The coordination geometry of the aluminium atoms deviates significantly from an ideal tetrahedron. On one side the angles O–Al–O are much smaller than tetrahedral and fall in the range between  $96.8(1)^\circ$  to  $103.4(1)^\circ$ , which is similar to  $(\text{MeOAlCl}_2)_3$  with the same parameter covering the range from  $95.4$  to  $100.4^\circ$  [7]. On the other side the Cl–Al–Cl angles are much larger than tetrahedral and found between  $113.3(1)^\circ$  and  $117.7(1)^\circ$ . The O–Al–Cl angles are scattered between  $106.3(1)^\circ$  and  $112.0(1)^\circ$ , *i.e.* close to the tetrahedral reference value.

The hydrogen bond between the hydroxy group and the chlorine atom Cl10 has a length of  $2.448$  Å (H $\cdots$ O), complemented by a short O–H bond of only  $0.68(3)$  Å and an O–H $\cdots$ Cl angle of  $166^\circ$  (O1 $\cdots$ Cl10  $3.117$  Å).

Further even longer hydrogen bonded contacts are observed between hydrogen atoms of the

methyl groups and chlorine atoms of other molecules with distances  $\text{H}\cdots\text{Cl}$  of 2.863 and 2.891 Å (Fig. 2). These contacts occur between two  $[(\text{MeOAlCl}_2)_3]$  units and between two  $[(\text{MeOAlCl}_2)_2(\text{HOAlCl}_2)]$  rings, but not between the two different  $\text{Al}_3\text{O}_3$  ring systems. This leads to an aggregation into an endless chain of molecules of the type AABBAABB, with two  $\text{C-H}\cdots\text{Cl}$  contacts within AA and BB units and the AB units linked by one  $\text{H}\cdots\text{Cl}$  bridge.

### Experimental Section

A solution of  $\text{MeAlCl}_2$  ( $1 \text{ mol l}^{-1}$  in hexanes) initially kept under dry nitrogen was placed in a vessel loosely closed so that air could slowly diffuse in. After four month crystals of  $[(\text{MeOAlCl}_2)_3]-[(\text{MeOAlCl}_2)_2(\text{HOAlCl}_2)]$  were found under the remaining  $(\text{MeAlCl}_2)_2$  solution, which were separated by decanting and dried with filter paper under a flow of nitrogen gas and characterised by X-ray crystallography and elemental analysis:  $M_r = 759.50 \text{ g mol}^{-1}$ , calcd. C 7.91 H 2.12, found C 7.76, H 2.21. The same material was found in commercial  $\text{MeAlCl}_2$  when air was not rigorously excluded during prolonged time of storage.

#### Crystal structure determination of $[(\text{MeOAlCl}_2)_3][(\text{MeOAlCl}_2)_2(\text{HOAlCl}_2)]$

Data collection was performed on a Nonius DIP2020 diffractometer.  $\text{C}_5\text{H}_{16}\text{Al}_6\text{Cl}_{12}\text{O}_6$   $M_r =$

759.46, crystal system triclinic, space group  $P\bar{1}$ ,  $Z = 2$ ,  $a = 8.8004(2)$ ,  $b = 9.9688(2)$ ,  $c = 18.9716(4)$  Å,  $\alpha = 99.6412(9)$ ,  $\beta = 91.5540(9)$ ,  $\gamma = 112.3639(9)^\circ$ ,  $V = 1509.89(6)$  Å<sup>3</sup> at 143(2) K,  $\mu = 1.294 \text{ mm}^{-1}$ ,  $2\theta_{\text{max}} = 60^\circ$ , 51034 scattering intensities collected, 7655 independent reflections ( $R_{\text{int}} = 0.029$ ). 276 parameters,  $R_1 = 0.0279$  for 6885 scattering intensities with  $F_o > 4\sigma(F_o)$  and  $wR_2 = 0.1160$  for all 7655 data. Intensity correction was applied by means of the program SCALEPACK [8]. Solution by direct methods and refinement of the structure was undertaken with the program SHELXTL 5.01 [9]. Hydrogen atoms were refined with isotropic displacement parameters using a ring model with fixed tetrahedral angles for the methyl groups and the C–H distances refined groupwise for each methyl group. The hydrogen atom of the hydroxy function was freely refined with an isotropic thermal parameter. All other atoms were refined anisotropically. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-204780. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).

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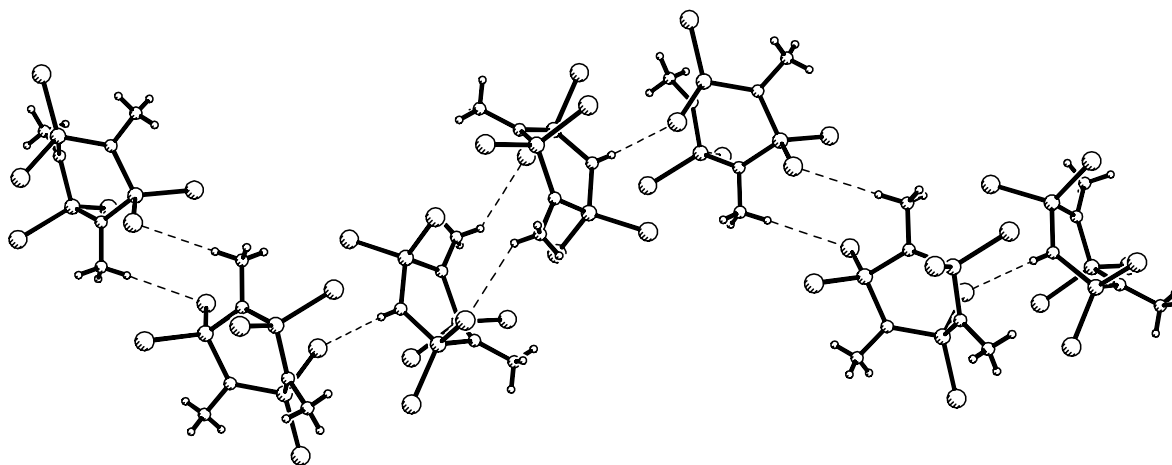


Fig. 2. Aggregation of  $[(\text{MeOAlCl}_2)_3][(\text{MeOAlCl}_2)_2(\text{HOAlCl}_2)]$  into an AABBAABB motif (A =  $[(\text{MeOAlCl}_2)_3]$ , B =  $[(\text{MeOAlCl}_2)_2(\text{HOAlCl}_2)]$ ) by hydrogen bonds of the type  $\text{C-H}\cdots\text{Cl}$  and  $\text{O-H}\cdots\text{Cl}$ .

- [1] H. Lehmkuhl, d K. Ziegler, in E. Müller (ed.): *Methoden Org. Chem.* (Houben-Weyl) Bd. XIII/4, Thieme-Verlag, Stuttgart (1970); E. A. Jeffrey, in *Organoaluminium Compounds*, Chapter 8, Elsevier, Amsterdam (1972); A. G. Davis, in D. Swern (ed.): *Organic Peroxides*, Vol. 2, Chapter 4, Wiley, London (1971).
- [2] J. Lewiński, J. Zachara, P. Goś, E. Grabska, T. Kopeć, I. Madura, W. Marciniak, I. Prowotorow, *Chem. Eur. J.* **6**, 3215 (2000).
- [3] A. Pasynkiewicz, *Polyhedron* **9**, 429 (1990).
- [4] H. W. Roesky, M. G. Walawalkar, R. Murugavel, *Acc. Chem. Res.* **34**, 201 (2001).
- [5] M. R. Mason, J. M. Smith, S. G. Bott, A. R. Barron, *J. Am. Chem. Soc.* **115**, 4971 (1993).
- [6] C. C. Landry, C. J. Harlan, S. G. Bott, A. R. Barron, *Angew. Chem.* **107**, 1315 (1995).
- [7] T. Gelbrich, U. Dümichen, P. Jörcchel, *Acta Cryst. Sect. C* **55**, 856 (1999).
- [8] Z. Otwinowski, W. Minor, *Methods Enzymol.* **276**, 307 (1976).
- [9] SHELXTL 5.01, Siemens Analytical X-Ray Instrumentation Inc. Madison, WI (1995).