

Communication

Reaction of methyl aluminium-(2,2'-methylene-*p*-chloro-bisphenoxide) with 2,2'-di(hydroxymethyl)biphenyl: A new aluminium complex bearing two kinds of diolate ligands

Wanda Ziemkowska^{a,*}, Magdalena Metelska^a, Przemysław Kruk^a,
Romana Anulewicz-Ostrowska^b

^a *Warsaw University of Technology, Faculty of Chemistry, Koszykowa 75, 00-662 Warsaw, Poland*

^b *Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland*

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Dedicated to Professor T.M. Krygowski on the occasion of his 70th birthday.

Abstract

A reaction of Me₃Al with 2,2'-methylene-*p*-chloro-bisphenol in Et₂O yielded Me₃Al₃[OC₆H₃(Cl)CH₂C₆H₃(Cl)O]₂ (**1**). Compound **1** reacted with 2,2'-di(hydroxymethyl)biphenyl to form Me₃Al₃[OC₆H₃(Cl)CH₂C₆H₃(Cl)O](OCH₂C₁₂H₈CH₂O)₂ (**2**) bearing two kinds of diolate ligands. Compound **2** was structurally characterised.

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Keywords: Aluminium; Diols; Alkoxides; Bisphenoxides; 2,2'-Di(hydroxymethyl)biphenyl

1. Introduction

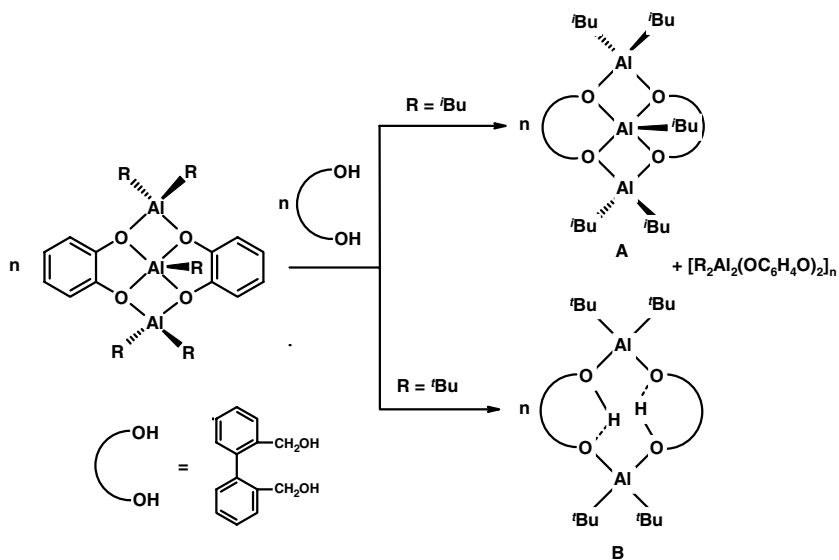
Alkyl aluminium (2,2'-methylene-bisphenoxides) play an important role as catalysts for the ring opening polymerisation (ROP) of cyclic esters and organic syntheses. ROP of cyclic esters such as DL-lactide and ϵ -caprolactone provides access to a class of biodegradable polyesters that have numerous pharmaceutical, biomedical and agricultural applications. During the last decade, aluminium 2,2'-methylene-bisphenoxides have been extensively studied by Lin [1–7], Okuda et al. [8] and Lewiński et al. [9] in the polymerisation of lactones, ϵ -caprolactone and lactides, in Diels–Alder coupling reactions and in the Meerwein–Ponndorf–Verley reduction. It has recently been shown by Zevaco et al. [10] that ethyl aluminium 2,2'-methylene-*p*-chloro-bisphenoxides are highly active in

the ROP of cyclohexene oxide and in the copolymerisation of cyclohexene oxide with CO₂. New aluminium complexes for special purposes, such as catalysis of organic syntheses and polymerisation, are still in demand.

Trinuclear alkylaluminium diolates of the general formula R₃Al₃[diol-(2H)]₂ are potentially reactive towards alcohols and water due to the presence of alkyl groups bonded to aluminium atoms. However, this method of synthesis of new complexes remains largely unexplored. Recently, we have found that alkyl aluminium 1,2-catecholates, R₃Al₃(OC₆H₄O)₂, react with diols formally eliminating R₃Al as new alkyl aluminium diolates **A** (R = *i*Bu) and **B** (R = *i*Bu) (Scheme 1) [11]. Reactions of alkyl aluminium benzopinacolates, R₃Al₃[OC(C₆H₅)₂C(C₆H₅)₂O]₂, with water and alcohols result in the formation of unusual dinuclear complexes R₂Al₂[OC(C₆H₅)₂C(C₆H₅)₂O]₂(C₄H₈O) (where R = Me, Et), which are active in the polymerisation of ϵ -caprolactone [12,13]. In this paper, we report a reaction of a trinuclear methyl aluminium (2,2'-methylene-*p*-chloro-bisphenoxide) complex with 2,2'-di(hydroxymethyl)-

* Corresponding author. Tel.: +48 22 6607316; fax: +48 22 6605462.

E-mail address: ziemk@ch.pw.edu.pl (W. Ziemkowska).



Scheme 1.

biphenyl leading to an aluminium compound bearing two kinds of diolate ligands.

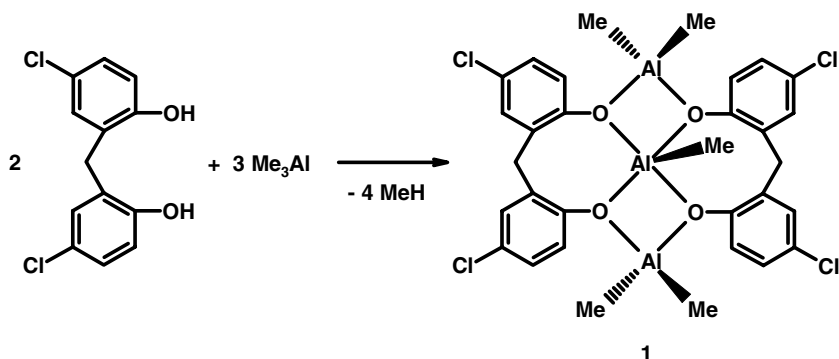
2. Results and discussion

Colourless methyl aluminium-(2,2'-methylene-*p*-chloro-bisphenoxide), $\text{Me}_5\text{Al}_3[\text{OC}_6\text{H}_3(\text{Cl})\text{CH}_2\text{C}_6\text{H}_3(\text{Cl})\text{O}]_2$ (**1**) was prepared as shown in Scheme 2.

Although proper crystals of **1** were not grown for X-ray measurements, we proposed the trinuclear structure of the compound on the basis of the well-documented structure of the ethyl aluminium derivative $\text{Et}_5\text{Al}_3[\text{OC}_6\text{H}_3(\text{Cl})\text{CH}_2\text{C}_6\text{H}_3(\text{Cl})\text{O}]_2$ [10]. According to our studies [14], methyl and ethyl aluminium diolates exhibit the same structures. Compound **1** was characterised by ^1H and ^{13}C NMR spectra in CDCl_3 and by elemental analysis. The ^1H NMR spectrum of **1** revealed three singlets of CH_3Al group protons (at -0.59 , -0.79 , and -1.14 ppm) and a doublet of methylene bridge protons (δ_{A} 4.20 and δ_{B} 3.53 ppm, $^2J_{\text{HH}} = 14.2$ Hz) with an integration ratio of

6:3:6:2:2, which was in agreement with the proposed structure. The singlet at -0.79 ppm was assigned to the protons of the methyl group bonded to the central aluminium atom. The protons of the four CH_3 groups attached to the peripheral aluminium atoms showed singlets at -0.59 and -1.14 ppm. One of the singlets was assigned to two magnetically equivalent AlCH_3 groups positioned *syn* to the methyl group bonded to the central aluminium atom. Similarly, one of the above-mentioned resonances was afforded by the protons of the two equivalent *anti* AlCH_3 groups. The ^{13}C NMR spectrum revealed one signal (at 32.76 ppm) of the CH_2 bridge carbons of the diolate units, indicating that the two methylene groups were equivalent in solution. Similarly to the ethyl aluminium-(2,2'-methylene-*p*-chloro-bisphenoxide) reported by Zevaco et al. [10], the ^{13}C NMR spectrum of **1** exhibited twelve aromatic carbon signals (see Section 3).

The reaction of **1** with 1 equiv. of 2,2'-di(hydroxymethyl)biphenyl in THF and toluene afforded a mixture of products, from which a white compound,



Scheme 2.

$\text{Me}_3\text{Al}_3[\text{OC}_6\text{H}_3(\text{Cl})\text{CH}_2\text{C}_6\text{H}_3(\text{Cl})\text{O}](\text{OCH}_2\text{C}_{12}\text{H}_8\text{CH}_2\text{O})_2 \cdot (\text{C}_6\text{H}_5\text{CH}_3) [2 \cdot (\text{C}_6\text{H}_5\text{CH}_3)]$, insoluble in *n*-hexane, was isolated in 91% yield (based on 2,2'-di(hydroxymethyl)biphenyl) (Scheme 3).

In contrast to the reactions of alkyl aluminium benzopinacولات and 1,2-catecholates with water, alcohols and diols [11–13], the reaction of **1** with 2,2'-di(hydroxymethyl)biphenyl proceeds without the elimination of R_3Al .

The molecular structure of $2 \cdot (\text{C}_6\text{H}_5\text{CH}_3)$ is shown in Fig. 1. Data collection and structure analysis are listed in Table 1. One molecule of $\text{C}_6\text{H}_5\text{CH}_3$ is present in the formula unit of **2**. The molecule of **2** consists of three diolate units (two $\text{OCH}_2\text{C}_{12}\text{H}_8\text{CH}_2\text{O}$ units originating from 2,2'-di(hydroxymethyl)biphenyl and one 2,2'-methylene-*p*-chloro-bisphenolate unit) bonded to three aluminium atoms. Each of the terminal four-coordinate aluminium atoms, Al(1) and Al(3), is bonded to three oxygen atoms (two oxygen atoms of the $\text{OCH}_2\text{C}_{12}\text{H}_8\text{CH}_2\text{O}$ units and one oxygen atom of the 2,2'-methylene-*p*-chloro-bisphenolate unit) and one methyl group. The central five-coordinate aluminium atom Al(2) is bonded to four oxygen atoms [O(3), O(4), O(5) and O(6)] of the $\text{OCH}_2\text{C}_{12}\text{H}_8\text{CH}_2\text{O}$ units and one methyl group. All methyl groups bonded to the aluminium atoms are situated *syn* to each other. The six Al–O bonds range from 1.713 Å to 1.963 Å. The bonds of the 2,2'-ethylene-*p*-chloro-bisphenoxide ligand, Al(1)–O(1) and Al(3)–O(2), are *ca.* 0.2 Å shorter than those to the $\text{OCH}_2\text{C}_{12}\text{H}_8\text{CH}_2\text{O}$ ligands.

The molecule of **2** adopts a distorted trigonal bipyramidal geometry around the central five-coordinate aluminium atom Al(2), with O(3) and O(6) occupying the axial positions [O(3)–Al(2)–O(6) = 157.5(1)°] and C(7), O(4) and O(5) defining the equatorial sites.

The ^1H NMR spectrum for **2** revealed two singlets at –0.15 [CH_3Al (terminal)] and –1.46 ppm [CH_3Al (central)] with an integration ratio of 2:1, indicating that the two methyls attached to the terminal aluminium atoms were equivalent in solution. This contrasts with the measured solid-state structure, in which the two methyls [C(6)H₃

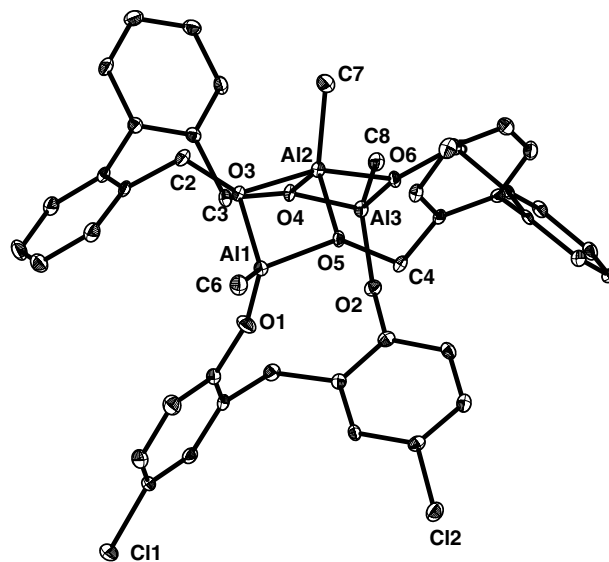
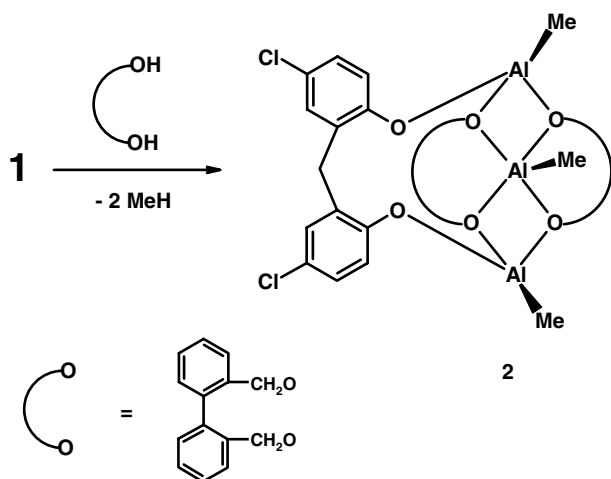


Fig. 1. Molecular structure of $\text{Me}_3\text{Al}_3[\text{OC}_6\text{H}_3(\text{Cl})\text{CH}_2\text{C}_6\text{H}_3(\text{Cl})\text{O}](\text{OCH}_2\text{C}_{12}\text{H}_8\text{CH}_2\text{O})_2$ (**2**). Thermal ellipsoids are shown at the 30% level. Hydrogen atoms and the molecule of $\text{C}_6\text{H}_5\text{CH}_3$ have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Al(1)–O(1) 1.713(2), Al(1)–O(3) 1.802(2), Al(1)–O(5) 1.824(2), Al(1)–C(6) 1.941(3), Al(2)–O(4) 1.857(2), Al(2)–O(5) 1.861(2), Al(2)–O(3) 1.941(2), Al(2)–O(6) 1.963(2), Al(2)–C(7) 1.949(3), Al(3)–O(2) 1.725(2), Al(3)–O(6) 1.813(2), Al(3)–O(4) 1.816(2), Al(3)–C(8) 1.943(3), O(4)–Al(2)–O(5) 112.1(1), O(4)–Al(2)–O(3) 91.0(1), O(5)–Al(2)–O(3) 76.6(1), O(4)–Al(2)–C(7) 125.0(1), O(5)–Al(2)–C(7) 123.0(1), O(3)–Al(2)–C(7) 100.7(1), O(4)–Al(2)–O(6) 75.7(1), O(5)–Al(2)–O(6) 91.4(1), O(3)–Al(2)–O(6) 157.5(1), C(7)–Al(2)–O(6) 101.8(1).

Table 1
Crystal data and data collection parameters for $2 \cdot (\text{C}_6\text{H}_5\text{CH}_3)$

	$2 \cdot (\text{C}_6\text{H}_5\text{CH}_3)$
Empirical formula	$\text{C}_{44}\text{H}_{41}\text{Al}_3\text{Cl}_2\text{O}_6 \cdot \text{C}_7\text{H}_8$
Formula weight	909.74
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
<i>a</i> (Å)	11.531(1)
<i>b</i> (Å)	13.141(1)
<i>c</i> (Å)	16.436(2)
α (°)	70.58(1)
β (°)	86.90(1)
γ (°)	77.28(1)
<i>V</i> (Å ³)	2290.6(5)
<i>Z</i>	2
<i>D</i> _{calc} (g cm ^{−3})	1.319
Absorption coefficient (mm ^{−1})	0.249
<i>F</i> (000)	952
Crystal size (mm)	0.20 × 0.20 × 0.15
θ range for data collection (°)	2.63 to 25.00
Index ranges	−13 ≤ <i>h</i> ≤ 13, −15 ≤ <i>k</i> ≤ 15, −19 ≤ <i>l</i> ≤ 19
Reflections collected	35379
Independent reflections [<i>R</i> _{int}]	8061 [0.0942]
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	8061/0/563
Goodness-of-fit on <i>F</i> ²	0.889
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0407, <i>wR</i> ₂ = 0.0648
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1017, <i>wR</i> ₂ = 0.0760
Maximum/Minimum of residual electron density	0.387 and −0.500



Scheme 3.

and C(8)H₃] were inequivalent. The signal of the methylene bridge protons of the bisphenoxide ligand appeared as a singlet at 3.48 ppm, indicating an equivalence of the CH₂ protons, which is also in contrast with the solid-state structure.

Similarly to the product of the interaction of Me₃Al with 2,2'-di(hydroxymethyl)biphenyl [Me₃Al₃(OCH₂C₁₂H₈CH₂O)₂] [14], the eight CH₂O protons of the two (OCH₂-C₁₂H₈CH₂O) ligands exhibited a pattern of four doublets at 4.53 (δ_{A1}), 4.13 (δ_{B1}) and 4.24 (δ_{A2}), 4.18 (δ_{B2}) ppm, respectively. The presence of two signals of CH₂O carbons (at 63.47 and 62.09 ppm) in the ¹³C NMR spectrum indicated two kinds of CH₂O groups. The magnetic difference between the CH₂O groups stems from the molecular structure with two groups below and two groups above the molecular plane in solution. This observation contrasts with the solid-state structure, in which the four CH₂O units were inequivalent. The differences between the solid-state structure and the NMR observations indicated that the molecule of **2** was fluxional in solution, presumably adopting a symmetry a pseudo-twofold axis coinciding with the central Al–C bond.

In summary, we have demonstrated a synthetic strategy for the preparation of aluminium complexes bearing two kinds of diolate ligands. This procedure utilises the reaction of trinuclear complexes R₅Al₃[diol¹-(2H)]₂ with diols leading to products with the general formula R₃Al₃[diol¹-(2H)]_{3-x}[diol²-(2H)]_x (x = 1, 2). In addition to their potential catalytic activity in polymerisation, the products can be regarded as precursors for the preparation of tailored nanosized Al₂O₃ by means of pyrolysis and sol-gel methods, as they are aluminium alkoxides. There are numerous examples of transformation of alkoxy aluminium compounds into Al₂O₃ nanoparticles [15].

Further studies on reactions of group 13 diolates with diols will be continued.

3. Experimental

All manipulations were carried out using standard Schlenk techniques under an inert gas atmosphere. The solvents were distilled over a blue benzophenone-K complex. Me₃Al, 2,2'-di(hydroxymethyl)biphenyl and 2,2'-methylene-*p*-chloro-bisphenol were purchased from Aldrich. ¹H and ¹³C NMR spectra were recorded on a Mercury-400BB spectrometer. ¹H NMR spectra were recorded at 400.09 MHz. Chemical shifts were referenced to the residual proton signals of CDCl₃ (7.26 ppm). ¹³C NMR spectra were acquired at 100.60 MHz (standard: chloroform ¹³CDCl₃, 77.20 ppm). Hydrolysable Me groups for compounds **1** and **2** were determined by hydrolysis of the compound (0.2–0.3 g) using HNO₃ solution (10% concentrated, 5 cm³) and measurement of the volume of CH₄.

3.1. Synthesis of Me₃Al₃[OC₆H₃(Cl)CH₂C₆H₃(Cl)O]₂ (**1**)

A solution of Me₃Al (1.15 g, 16 mmol) in Et₂O (10 cm³) was added to a stirred solution of 2,2'-methylene-*p*-chloro-

bisphenol (2.69 g, 10 mmol) in Et₂O (30 cm³) at –76 °C. The reaction mixture was allowed to warm slowly to room temperature. Evolution of gases was observed during the course of the reaction. A white solid of complex **1** (2.93 g, 85% yield) precipitated immediately from the post-reaction mixture.

¹H NMR (CDCl₃): δ 7.33 (2H, d, ⁴J_{H–H} = 2.8 Hz, H_{aromat}), 7.24 – 7.15 (6H, m, H_{aromat}), 7.05 (2H, d, ³J_{H–H} = 8.8 Hz, H_{aromat}), 6.98 (2H, d, ³J_{H–H} = 8.8 Hz, H_{aromat}), δ_A 4.20, δ_B 3.53 [4H, dd, ²J_{H–H} = 14.2 Hz, CH₂], –0.59 (6H, s, AlCH₃), –0.79 (3H, s, AlCH₃), –1.14 (6H, s, AlCH₃). ¹³C NMR (CDCl₃) δ 150.74, 147.62, 131.29, 131.19, 131.09, 130.28, 129.89, 128.80, 128.38, 127.95, 120.43, 119.95 (C_{aromat}), 32.76 (CH₂), –8.35, –10.46 (AlCH₃) ppm.

Elemental Anal. Calc. for Me₃Al₃[OC₆H₃(Cl)CH₂-C₆H₃(Cl)O]₂: Al, 11.74; Me, 10.87 wt%. Found: Al, 11.52; hydrolysable methyl groups, 11.20.

3.2. Synthesis of Me₃Al₃[OC₆H₃(Cl)CH₂C₆H₃(Cl)O]-(OCH₂C₁₂H₈CH₂O)₂ · (C₆H₅CH₃)₂ · (C₆H₅CH₃)

A suspension of 2,2'-di(hydroxymethyl)biphenyl (0.43 g, 2 mmol) in C₆H₅CH₃ (5 cm³) was added to a stirred solution of **1** (1.38 g, 2 mmol) in THF (15 cm³) at –76 °C. The reaction mixture was allowed to warm to room temperature. Gases evolving in the reaction were collected in a burette (3.9 mmol of methane based on the volume of gases). The solvents were removed from the post-reaction mixture by distillation under reduced pressure. A mixture of *n*-C₆H₁₄ (10 cm³) and C₆H₅CH₃ (1 cm³) was added to the white solid resulting in a suspension. After filtration a white solid of **2** · C₆H₅CH₃ (0.83 g, 91% yield based on 2,2'-di(hydroxymethyl)biphenyl) was separated. The compound underwent decomposition at 170 °C without melting.

¹H NMR (CDCl₃): δ 7.53–7.03 (m, 21H, H_{aromat} of OCH₂C₁₂H₈CH₂O units and toluene), {[6.68 (d, ⁴J_{H–H} = 2.8 Hz, 2H, C³H_{aromat}), 6.62 (dd, ³J_{H–H} = 8.5 Hz, ⁴J_{H–H} = 2.8 Hz, 2H, C⁵H_{aromat}), 5.73 (d, ³J_{H–H} = 8.5 Hz, 2H, C⁶H_{aromat})] signals of the aromatic protons of 2,2'-methylene-4-chloro-bisphenolate unit}, 4.53 (δ_{A1}), 4.13 (δ_{B1}) (dd, ²J_{H–H} = 11.6 Hz, 4H, CH₂O, AB pattern), 4.24 (δ_{A2}), 4.18 (δ_{B2}) (dd, ²J_{H–H} = 12.8 Hz, 4H, CH₂O, AB pattern), 3.48 (s, 2H, CH₂), 2.36 (s, 3H, C₆H₅CH₃), –0.15 (s, 6H, Al_(4coord)CH₃), –1.46 (s, 3H, Al_(5coord)CH₃). ¹³C NMR (CDCl₃) δ 154.10, 141.15, 138.92, 136.89, 135.58, 130.93, 130.76, 130.00, 129.44, 129.26, 129.15, 129.11, 129.02, 128.91, 128.46, 126.26, 122.62, 119.75 (C_{aromat} of diolate units), 137.86, 129.02 (overlapping with the signal of diolate units), 128.21, 125.27 (C_{aromat} of C₆H₅CH₃) 63.47, 62.09 (CH₂O), 30.56 (CH₂), 21.60 (C₆H₅CH₃) ppm.

Elemental Anal. Calc. for {Me₃Al₃[OC₆H₃(Cl)CH₂-C₆H₃(Cl)O][OCH₂(C₆H₄)₂CH₂O]₂ · C₆H₅CH₃}: Al, 8.89; Me, 4.94 wt%. Found: Al, 8.70; hydrolysable methyl groups, 4.75.

A small amount of X-ray quality crystals were grown from a solution of **2** · C₆H₅CH₃ in *n*-C₆H₁₄ and C₆H₅CH₃ at 5 °C.

3.3. X-ray crystal structure analysis

A crystal of compound **2** · C₆H₅CH₃ was mounted in inert oil and sealed in a glass capillary under argon. Determination of the crystal structure of **2** was performed on a KUMA KM4CCD κ -axis diffractometer with graphite-monochromated Mo K α radiation. The crystal of **2** was positioned at 62.25 mm from the KM4CCD camera and 1200 frames were measured at 1.0° intervals with a counting time of 18 s. All of the data were corrected for Lorentz and polarisation effects. No absorption correction was applied. Data reduction and analysis were carried out using the KUMA Diffraction programs. The structure of the investigated crystal was solved by the direct methods [16] and refined using the SHELXL computer programs [17]. All hydrogen atoms were placed in the calculated positions and their thermal parameters were refined isotropically. The atomic scattering factors were taken from the International Tables [18].

The X-ray structures were measured in the Crystallography Unit of the Physical Chemistry Laboratory at the Chemistry Department of the University of Warsaw.

Acknowledgements

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Appendix A. Supplementary material

CCDC 654108 contains the supplementary crystallographic data for **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.11.033](https://doi.org/10.1016/j.jorganchem.2007.11.033).

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