Pentanuclear alkoxyaluminium hydrides

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Reaction of $[\mathrm{AlH_3(OEt_2)}]$ (generated *in situ* from $\mathrm{AlCl_3}$ and 3 equivalents of $\mathrm{LiAlH_4}$) with one equivalent of $\mathrm{Pr^iOH}$ resulted in the formation of the pentanuclear complex $[\mathrm{Al_5(\mu_4\text{-}O)(\mu\text{-}OPr^i)_7H_6}]$. Incomplete reaction of $\mathrm{AlCl_3}$ and 3 equivalents of $\mathrm{LiAlH_4}$, followed by the addition of $\mathrm{Pr^iOH}$, afforded the novel species $[\mathrm{Al_5(\mu_5\text{-}O)(\mu\text{-}OPr^i)_8(Cl)H_4}]$. Both complexes have been structurally characterised.

Introduction

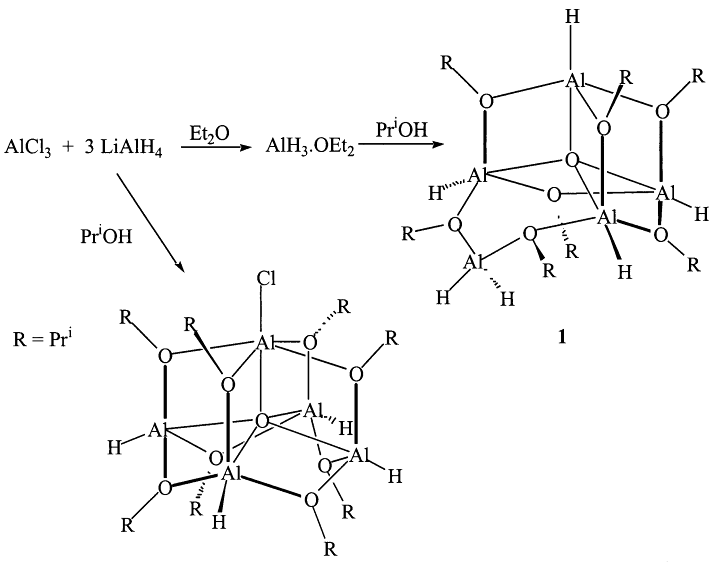
Thin films of aluminium oxide are of interest as optical filters, insulating layers, wear resistant coatings and corrosion protective coatings.[1–3] The versatility of metal alkoxides as convenient precursors to metal oxides *via* sol–gel and CVD (chemical vapour deposition) processes is widely recognised.[4] However, the application of aluminium alkoxides for the deposition of $\mathrm{Al_2O_3}$ thin films remains limited. Recently, the use of aluminium dimethylisopropoxide as a precursor for the CVD of alumina thin films was described.[5,6] The aluminium oxide films obtained were transparent and amorphous.

Alkoxyalanes, of the type $[\mathrm{(RO)}_n\mathrm{AlH}_{3-n}]$ (where $n = 1$ or 2), should be excellent precursors to metal or mixed-metal oxide films, due to the presence of the hydride ligand. This should minimise contamination from species such as carbon in the resulting material. The synthesis and structures of (*tert*-butoxy)alanes, of the type $[\mathrm{(Bu^tO)}_n\mathrm{AlH}_{3-n}]$ (where $n = 1$ or 2) have been described previously and were used in CVD processes, resulting in the formation of an aluminium/aluminium hydride-oxide composite.[7] Alkoxyalanes are also an interesting class of compound, due to the range of structural types that can be obtained.[7–9] These compounds are stabilised by association (dimerisation, oligomerisation or polymerisation) *via* the formation of oxo or hydride bridges.[8] For example, the complex $[\mathrm{Al_3(OPr^i)_4H_5}]$ has been isolated as a trinuclear complex with bridging alkoxide groups, and as a chain polymer in which the $[\mathrm{Al_3(OPr^i)_4H_5}]$ units are connected through hydride bridges.[9] With a view to extending the range of alkoxyalanes and obtaining more information about their structural diversity, we have carried out the reaction of alane with isopropanol under different conditions. Two new aluminium oxoalkoxides, namely $[\mathrm{Al_5(\mu_4\text{-}O)(\mu\text{-}OPr^i)_7H_6}]$ and $[\mathrm{Al_5(\mu_5\text{-}O)(\mu\text{-}OPr^i)_8(Cl)H_4}]$, have been synthesised and structurally characterised.

Results and discussion

The reaction between $[\mathrm{AlH_3(OEt_2)}]$ (generated *in situ* from $\mathrm{LiAlH_4}$ and $\mathrm{AlCl_3}$[8]) and 1 equivalent of $\mathrm{Pr^iOH}$ in diethyl ether at room temperature resulted, after work up, in the isolation of colourless crystalline **1** (Scheme 1). An X-ray structure determination showed that the pentanuclear complex $[\mathrm{Al_5(\mu_4\text{-}O)(\mu\text{-}OPr^i)_7H_6}]$ (**1**) had formed (Fig. 1), the molecule having crystallographic C_s symmetry about a plane containing Al(3), Al(4) and O(4). The geometry at the central, four-coordinate, oxygen atom can be visualised as being distorted square pyramidal, with Al(4) occupying the apical position, but with the basal site opposite to Al(3) vacant; the Al(2)–O–Al(2A) angle is 154.09(15)°, whilst the remaining Al–O–Al angles are in the range 97.88(8) to 99.02(8)°. The oxygen atom lies 0.26 Å out of the Al(2)/Al(2A)/Al(3) plane in the direction of Al(4). The Al–O(isopropoxide) distances involving Al(2), Al(3) and Al(4) are typical (Table 1), whereas those to the bridging $\mathrm{Al(1)H_2}$ unit are significantly shorter by 0.04 Å; conversely, the Al–O bonds to the central oxygen atom are 0.04 Å longer, with that to the "apical" aluminium Al(4) being the longest. The overall structure is similar to that of the tetranuclear aluminium complex $[\mathrm{Al_4(\mu_4\text{-}O)(\mu\text{-}OPr^i)_5(OPr^i)(Pr^iOH)Cl_4}]$,[10] but with the chlorides replaced by hydrides and the insertion of an $\mathrm{AlH_2}$ bridge between the pendant isopropanol-isopropoxy oxygen atoms instead of the O–H···O hydrogen bond (the O···O separation in the hydrogen bond is 2.47 Å, and this distance increases to 2.91 Å on insertion of the $\mathrm{AlH_2}$ unit). The Al–O distances in the tetra-aluminium complex are comparable to those observed in **1**. There are no intermolecular interactions of note.

Other previously reported oxoalkoxides of aluminium include $[\mathrm{Al_4(\mu\text{-}O)(OBu^i)_{11}H}]$,[11] $[\mathrm{Al_{10}(\mu_4\text{-}O)_2(\mu_3\text{-}O)_2(\mu\text{-}OEt)_{14}(OEt)_8}]$[12] and $[\mathrm{Al_5(\mu_5\text{-}O)(OBu^i)_8H_5}]$,[13] which were prepared by the hydrolysis of aluminium alkoxide precursors. Recently, the range of aluminium oxoalkoxides has been extended and the structures of $[\mathrm{Al_5(\mu_5\text{-}O)(\mu\text{-}OBu^i)_8(OBu^i)_5}]$ and $[\mathrm{Al_8(\mu_4\text{-}O)_2(\mu\text{-}OH)(\mu\text{-}OBu^i)_{10}(OBu^i)_8}]$ reported.[14] The current interest in metal oxoalkoxides is a result of these complexes being proposed as intermediates in the conversion of metal alkoxide precursors into metal oxides (*via* CVD or sol–gel techniques).[15] The formation of compound **1** could be the result of hydrolysis, however oxoalkoxides have resulted previously, even where exceptional precautions against adventitious hydrolysis were taken. For example, triisopropoxides of a number of metals are actually pentanuclear oxoaggregates of formula $[\mathrm{M_5(\mu_5\text{-}O)(\mu_3\text{-}OPr^i)_4(\mu\text{-}OPr^i)_4(OPr^i)_5}]$ (M = In, Sc, Yb, Nd, Sm, Gd, Pr).[16,17] Interestingly, the complex $[\mathrm{Al_3(OPr^i)_4H_5}]$, was also prepared from the reaction between $[\mathrm{AlH_3(OEt_2)}]$ and $\mathrm{Pr^iOH}$ in diethyl ether.[9] However, the reaction temperature employed to prepare compound **1** was higher (room temperature *vs.*



1

2

Scheme 1

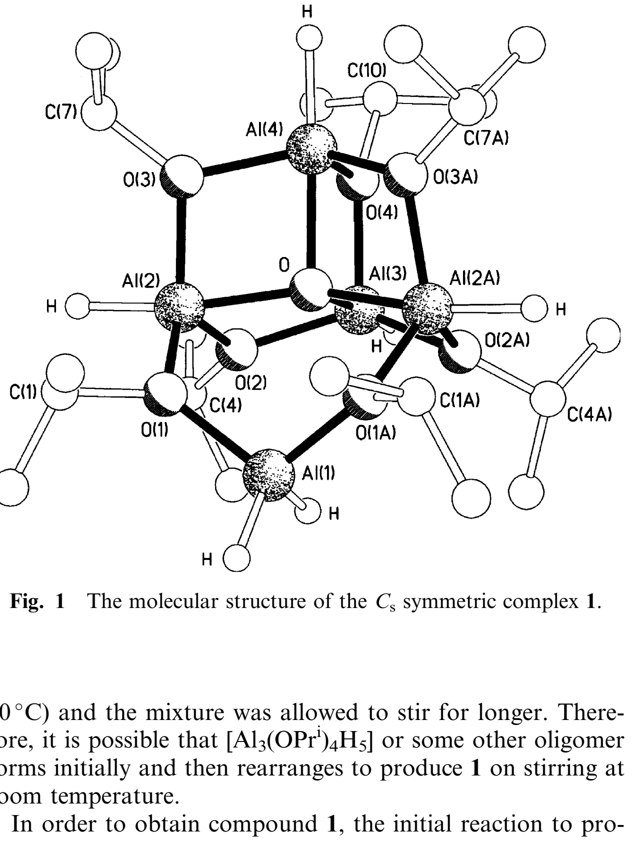


Fig. 1 The molecular structure of the C_s symmetric complex **1**.

10 °C) and the mixture was allowed to stir for longer. Therefore, it is possible that [Al$_3$(OPr^i)$_4$H$_5$] or some other oligomer forms initially and then rearranges to produce **1** on stirring at room temperature.

In order to obtain compound **1**, the initial reaction to produce [AlH$_3$(OEt$_2$)] (from LiAlH$_4$ and AlCl$_3$) was allowed to stir for 30 min before addition of isopropanol. However, if isopropanol is added immediately to the slurry of LiAlH$_4$ and AlCl$_3$ in diethyl ether, colourless crystals of a new compound (**2**) are obtained (Scheme 1).

An X-ray structure determination showed the crystals of **2** to contain two crystallographically independent C_2 symmetric penta-aluminium(III) cages, one of which is shown in Fig. 2 [the C_2 axis lies along the Cl–Al(1)–O vector]. By far the closest analogue of **2** to have been structurally characterised is [Al$_5$(μ_5-O)(OBu^i)$_8$H$_5$],[13] the only major difference between the two structures being in the apical site, which is occupied by a chloride in **2** and by an hydrido in the pentahydrido species. Both complexes have essentially identical "cage" structures, with the bonds from O(1), O(2), O(1A) and O(2A) to the apical aluminium Al(1) being *ca.* 0.15 Å longer than their counterparts to Al(2) and Al(3) (Table 2). Similarly, the basal O–Al(2), O–Al(3), O–Al(2A) and O–Al(3A) distances are *ca.* 0.15 Å longer than those between Al(1) and O(1), O(2), O(1A) and O(2A). The only significant difference between the two structures is the length of the O–Al(1) bond, which is 1.843(3) and 1.852 (4) Å in the two independent molecules of **2**, compared with 1.900(4) Å in the pentahydrido complex. Accompanying this change in bond length in **2** is a small reduction in the displacement of Al(1) from the O(1)/O(2)/O(1A)/O(2A) plane from 0.36 to 0.32 Å, and an increase from 0.26 to 0.28 Å in the deviation of O from the Al(2)/Al(3)/Al(2A)/Al(3A) plane. There are no noteworthy interactions beyond the molecule. The structure of compound **2** is also similar to that of the recently reported cluster [Al$_5$(μ_5-O)(μ-OBu^i)$_8$(OBu^i)$_5$],[14] which has an average Al(1)–O distance of 1.89 Å, similar to that observed in [Al$_5$(μ_5-O)(OBu^i)$_8$H$_5$].[13]

The ^{1}H NMR spectrum of **1** in C$_6$D$_6$ displays a number of overlapping multiplets corresponding to the methine groups (4.56–4.63 and 4.75 ppm) and the methyls (1.40–1.50 ppm) of the isopropyl ligands. These data suggest that the behaviour of **1** in solution is complicated and that the solid state structure is not retained (at room temperature). Similarly, the behaviour of **2** in C$_6$D$_6$ at room temperature is also complex. No signals due to the hydride ligands on the Al atoms were detected in the ^{1}H NMR spectra of **1** and **2**. However, the IR spectra of both **1** and **2** (KBr disks) showed characteristic absorption bands for Al–H stretching (**1**, 1830, 1822 cm^{-1}; **2**, 1820 cm^{-1}) and deformation (**1**, 784, 725 cm^{-1}; **2**, 769 cm^{-1}) modes.

Conclusions

Two pentanuclear alkoxyaluminium clusters (compounds **1** and **2**) have been prepared and structurally characterised. Compounds **1** and **2** were synthesised from the reaction of AlCl$_3$, three equivalents of LiAlH$_4$ and four equivalents of Pr^{i}OH in diethyl ether. However, in order to isolate **1**, it is necessary to allow the initial reaction between AlCl$_3$ and LiAlH$_4$ to proceed for a longer period of time.

Table 1 Selected bond lengths (Å) and angles (°) for compound **1**

Al(1)–O(1)	1.815(2)	Al(1)–O(1A)	1.815(2)	Al(2)–O(2)	1.843(2)
Al(2)–O(3)	1.850(2)	Al(2)–O(1)	1.851(2)	Al(2)–O	1.8873(9)
Al(2)–Al(4)	2.8859(12)	Al(2)–Al(3)	2.8900(12)	Al(3)–O(4)	1.853(4)
Al(3)–O(2A)	1.858(2)	Al(3)–O(2)	1.858(2)	Al(3)–O	1.913(3)
Al(3)–Al(2A)	2.8900(12)	Al(3)–Al(4)	2.907(2)	Al(4)–O(3A)	1.844(2)
Al(4)–O(3)	1.844(2)	Al(4)–O(4)	1.845(4)	Al(4)–O	1.940(3)
Al(4)–Al(2A)	2.8859(12)	O–Al(2A)	1.8873(9)		
O(1)–Al(1)–O(1A)	106.62(14)	O(2)–Al(2)–O(3)	119.97(11)	O(2)–Al(2)–O(1)	118.67(10)
O(3)–Al(2)–O(1)	116.44(10)	O(2)–Al(2)–O	78.48(10)	O(3)–Al(2)–O	78.68(10)
O(1)–Al(2)–O	90.97(10)	O(2)–Al(2)–Al(4)	94.80(8)	O(3)–Al(2)–Al(4)	38.55(6)
O(1)–Al(2)–Al(4)	116.15(8)	O–Al(2)–Al(4)	41.75(8)	O(2)–Al(2)–Al(3)	38.84(7)
O(3)–Al(2)–Al(3)	95.64(7)	O(1)–Al(2)–Al(3)	115.96(8)	O–Al(2)–Al(3)	40.82(8)
Al(4)–Al(2)–Al(3)	60.45(4)	O(4)–Al(3)–O(2A)	107.47(8)	O(4)–Al(3)–O(2)	107.47(8)
O(2A)–Al(3)–O(2)	131.8(2)	O(4)–Al(3)–O	79.44(13)	O(2A)–Al(3)–O	77.47(7)
O(2)–Al(3)–O	77.47(7)	O(4)–Al(3)–Al(2A)	87.88(9)	O(2A)–Al(3)–Al(2A)	38.46(7)
O(2)–Al(3)–Al(2A)	112.27(8)	O–Al(3)–Al(2A)	40.16(3)	O(4)–Al(3)–Al(2)	87.88(9)
O(2A)–Al(3)–Al(2)	112.27(8)	O(2)–Al(3)–Al(2)	38.46(7)	O–Al(3)–Al(2)	40.16(3)
Al(2A)–Al(3)–Al(2)	79.05(4)	O(4)–Al(3)–Al(4)	38.08(10)	O(2A)–Al(3)–Al(4)	93.76(8)
O(2)–Al(3)–Al(4)	93.76(8)	O–Al(3)–Al(4)	41.36(8)	Al(2A)–Al(3)–Al(4)	59.71(3)
Al(2)–Al(3)–Al(4)	59.71(3)	O(3A)–Al(4)–O(3)	126.8(2)	O(3A)–Al(4)–O(4)	110.04(8)
O(3)–Al(4)–O(4)	110.04(8)	O(3A)–Al(4)–O	77.48(7)	O(3)–Al(4)–O	77.48(7)
O(4)–Al(4)–O	78.93(13)	O(3A)–Al(4)–Al(2A)	38.69(7)	O(3)–Al(4)–Al(2A)	111.06(8)
O(4)–Al(4)–Al(2A)	88.15(9)	O–Al(4)–Al(2A)	40.38(3)	O(3A)–Al(4)–Al(2)	111.06(8)
O(3)–Al(4)–Al(2)	38.69(7)	O(4)–Al(4)–Al(2)	88.15(9)	O–Al(4)–Al(2)	40.38(3)
Al(2A)–Al(4)–Al(2)	79.18(4)	O(3A)–Al(4)–Al(3)	95.20(8)	O(3)–Al(4)–Al(3)	95.20(8)
O(4)–Al(4)–Al(3)	38.27(11)	O–Al(4)–Al(3)	40.66(8)	Al(2A)–Al(4)–Al(3)	59.85(3)
Al(2)–Al(4)–Al(3)	59.85(3)	Al(2A)–O–Al(2)	154.1(2)	Al(2A)–O–Al(3)	99.02(8)
Al(2)–O–Al(3)	99.02(8)	Al(2A)–O–Al(4)	97.88(8)	Al(2)–O–Al(4)	97.88(8)
Al(3)–O–Al(4)	97.99(12)	Al(1)–O(1)–Al(2)	117.98(11)	Al(2)–O(2)–Al(3)	102.70(10)
Al(4)–O(3)–Al(2)	102.76(10)	Al(4)–O(4)–Al(3)	103.6(2)		

Experimental

General procedures

All manipulations were performed under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques or in a Mbraun Unilab glove box. All solvents were distilled from appropriate drying agents prior to use (sodium–benzophenone for diethyl ether). [$AlH_3(OEt_2)$][8] was prepared *in situ* by literature methods. All other reagents were procured commercially from Aldrich and used without further purification. Microanalytical data were obtained at University College London (UCL).

Physical measurements

Syntheses

^{1}H and ^{13}C NMR spectra were recorded on Brüker AMX400 spectrometer at UCL, referenced to C_6D_6, which was degassed and dried over molecular sieves prior to use; ^{1}H and ^{13}C chemical shifts are reported relative to $SiMe_4$ (δ 0.00). FT-IR spectra were run on a Shimadzu FTIR-8200 instrument. Melting points were obtained in sealed glass capillaries under nitrogen and are uncorrected.

[$Al_5(\mu_4\text{-}O)(\mu\text{-}OPr^i)_7H_6$] 1. Following literature routes,[8] $AlCl_3$ (0.59 g, 4.39 mmol) was dissolved in diethyl ether (10 cm^3) and added slowly to a stirred slurry of $LiAlH_4$ (0.50 g, 13.2 mmol) in diethyl ether (10 cm^3). After stirring for 30 min, Pr^{i}OH (1.34 cm^3, 17.6 mmol) was added dropwise to this mixture and the immediate evolution of hydrogen was observed. The resulting grey slurry was stirred at room temperature for 4 h. After filtering through Celite, the solvent was reduced *in vacuo* to approximately 5 cm^3 and cooled to −20 °C. After a period of time at this temperature, colourless crystals of **1** formed (m.p. 190–193 °C; yield 0.54 g, 43%). Anal. calc. for $C_{21}H_{55}O_8Al_5$: C, 44.21; H, 9.72; found C, 43.51; H, 9.03%. ^{1}H NMR (C_6D_6): δ 1.40–1.50 [m, OCH(C*H*$_3$)$_2$], 4.46–4.63 [m, OC*H*(CH$_3$)$_2$], 4.75 [spt, OC*H*(CH$_3$)$_2$], Al*H* not detected. ^{13}C{^{1}H} NMR (C_6D_6): δ 23.7, 24.6, 25.0, 25.3 [s, OCH(*C*H$_3$)$_2$], 66.3, 66.9 [s, O*C*H(CH$_3$)$_2$]. IR (KBr disk): 2975s, 2930m, 2874w, 1830w, 1822m br, 1719w, 1454w, 1376m, 1262w, 1175m, 1130s, 1132s, 977s, 946m, 840s, 784s, 725s, 647s, 566w, 532m cm^{-1}.

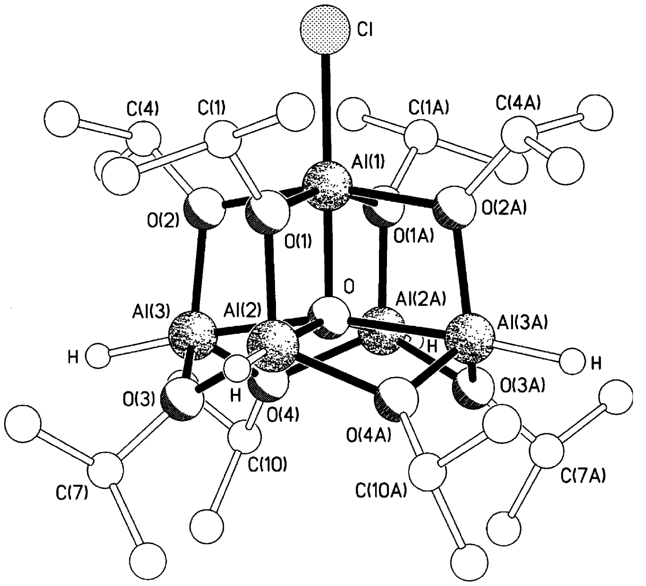


Fig. 2 The molecular structure of the one of the pair of crystallographically independent C_2 symmetric Al_5 cages present in the crystals of **2**.

[$Al_5(\mu_5\text{-}O)(\mu\text{-}OPr^i)_8(Cl)H_5$] 2. Compound **2** was prepared using the same procedure described above for **1**, except that

Table 2 Selected bond lengths (Å) and angles (°) for the two crystallographically independent molecules (**A** and **B**) in the structure of **2**

	A	**B**		**A**	**B**
Al(1)–Cl	2.188(2)	2.184(3)	Al(1)–O	1.843(4)	1.852(4)
Al(1)–O(1)	1.950(3)	1.963(3)	Al(1)–O(2)	1.964(3)	1.937(3)
Al(2)–O	2.062(1)	2.177(2)	Al(2)–O(1)	1.813(3)	1.810(3)
Al(2)–O(3)	1.826(3)	1.817(3)	Al(2)–O(4A)	1.830(3)	1.814(3)
Al(3)–O	2.126(1)	2.006(1)	Al(3)–O(2)	1.816(3)	1.817(3)
Al(3)–O(3)	1.828(3)	1.833(3)	Al(3)–O(4)	1.817(3)	1.839(3)
Cl–Al(1)–O	180.0	180.0	Cl–Al(1)–O(1)	99.63(9)	98.78(10)
Cl–Al(1)–O(2)	99.10(9)	100.08(10)	O–Al(1)–O(1)	80.37(9)	81.22(10)
O–Al(1)–O(2)	80.90(9)	79.92(10)	O(1)–Al(1)–O(1A)	160.7(2)	162.4(2)
O(1)–Al(1)–O(2)	88.17(12)	88.43(12)	O(1)–Al(1)–O(2A)	88.80(12)	88.51(12)
O(2)–Al(1)–O(2A)	161.8(2)	159.8(2)	O–Al(2)–O(1)	78.10(14)	76.5(2)
O–Al(2)–O(3)	78.49(11)	75.88(12)	O–Al(2)–O(4A)	78.88(10)	75.94(12)
O(1)–Al(2)–O(3)	110.80(14)	116.0(2)	O(1)–Al(2)–O(4A)	115.34(14)	109.8(2)
O(3)–Al(2)–O(4A)	122.18(14)	117.4(2)	O(2)–Al(3)–O	77.23(14)	78.9(2)
O(3)–Al(3)–O	76.79(10)	80.04(12)	O(4)–Al(3)–O	77.48(10)	79.90(12)
O(2)–Al(3)–O(3)	116.48(14)	109.3(2)	O(2)–Al(3)–O(4)	109.64(14)	115.5(2)
O(3)–Al(3)–O(4)	119.42(14)	125.6(2)	Al(1)–O–Al(2)	98.05(11)	96.32(11)
Al(1)–O–Al(3)	97.36(10)	98.59(12)	Al(2)–O–Al(2A)	163.9(2)	167.4(2)
Al(2)–O–Al(3)	88.94(5)	88.99(6)	Al(2)–O–Al(3A)	89.00(5)	89.12(6)
Al(3)–O–Al(3A)	165.3(2)	162.8(2)	Al(1)–O(1)–Al(2)	103.29(14)	105.8(2)
Al(1)–O(2)–Al(3)	104.35(14)	102.4(2)	Al(2)–O(3)–Al(3)	106.83(14)	107.0(2)
Al(3)–O(4)–Al(2A)	107.20(14)	107.0(2)			

Pr^iOH was added immediately to the slurry of $LiAlH_4$ and $AlCl_3$. Colourless crystals of **2** formed from a concentrated diethyl ether solution at −20 °C (m.p. 82–84 °C; yield 0.51g, 39%). Anal. calc. for $C_{24}H_{60}ClO_9Al_5$: C, 43.47; H, 9.12; found C, 44.27; H, 9.40%. ^1H NMR (C_6D_6): δ 1.32–1.48 [m, 24H, $OCH(CH_3)_2$], 4.20spt, 4.35spt, 4.58spt, 4.76spt [ratio 1:1:2:2, $OCH(CH_3)_2$], Al*H* not detected. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 25.2, 25.4, 28.1, 28.2 [s, $OCH(CH_3)_2$], 63.7, 66.9, 67.5, 67.9 [s, $OCH(CH_3)_2$]. IR (KBr disk): 2971s, 2931m, 2875w, 1820m br, 1384m, 1375m, 1270w, 1175m, 1128s, 1010w, 965s, 844m, 824sh, 769m, 669s cm^{-1}.

Single crystal X-ray analysis

Crystal data for 1. $C_{21}H_{55}O_8Al_5$, $M = 570.6$, orthorhombic, *Pnma* (no. 62), $a = 11.820(1)$, $b = 18.129(2)$, $c = 15.745(1)$ Å, $V = 3373.8(5)$ $Å^3$, $Z = 4$ (C_s symmetry), $D_c = 1.123$ g cm^{-3}, μ(Cu-Kα) = 18.3 cm^{-1}, $T = 183$ K, colourless platy needles; 2553 independent measured reflections, F^2 refinement, $R_1 = 0.049$, $wR_2 = 0.131$, 1946 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 120°$], 195 parameters.

Crystal data for 2. $C_{24}H_{60}ClO_9Al_5$, $M = 663.1$, monoclinic, *P*2/*c* (no. 13), $a = 20.331(2)$, $b = 9.382(1)$, $c = 20.680(2)$ Å, $\beta = 109.25(1)°$, $V = 3723.9(6)$ $Å^3$, $Z = 4$ (two independent C_2 symmetric molecules), $D_c = 1.183$ g cm^{-3}, μ(Cu-Kα) = 23.9 cm^{-1}, $T = 183$ K, colourless prisms; 5530 independent measured reflections, F^2 refinement, $R_1 = 0.066$, $wR_2 = 0.184$, 4496 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 120°$], 372 parameters.

CCDC reference numbers 183238 and 183239. See http://www.rsc.org/suppdata/nj/b2/b201773n/ for crystallographic data in CIF or other electronic format.

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