DALTON
FULL PAPER

New polynuclear aluminium oxoalkoxides. Crystal structures of $[Al_5(\mu_5\text{-}O)(\mu\text{-}OBu^i)_8(OBu^i)_5]$ and $[Al_8(\mu_4\text{-}O)_2(\mu\text{-}OH)_2(\mu\text{-}OBu^i)_{10}(OBu^i)_8]$

Isaac Abrahams,*[a] Donald C. Bradley,*[a] Halina Chudzynska,[a] Majid Motevalli[a] and Robin A. Sinclair[b]

[a] *Department of Chemistry Queen Mary, University of London, Mile End Road, London, UK E1 4NS. E-mail: i.abrahams@qmul.ac.uk*
[b] *Ceramic Technology Center, 3M, St. Paul Minnesota, 5514-1000, USA*

Received 3rd July 2001, Accepted 14th November 2001
First published as an Advance Article on the web 20th December 2001

Treatment of $[Al_4(\mu_4\text{-}O)(OBu^i)_{10}(Bu^iOH)]$ **1** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in boiling toluene produced $[Al_5(\mu_5\text{-}O)(\mu\text{-}OBu^i)_8(OBu^i)_5]$ **2**, whereas removal of Bu^iOH from **1** by azeotropic fractional distillation with toluene gave $[Al_8(\mu_4\text{-}O)_2(\mu\text{-}OH)_2(\mu\text{-}OBu^i)_{10}(OBu^i)_8]$ **3**. X-Ray crystallography revealed that in **2** the μ_5-oxo atom is bonded to one apical six-coordinated Al and four basal five-coordinated Al atoms, whilst in **3** the centrosymmetrical molecule comprises two tetranuclear fragments each containing a μ_4-oxo atom bonded to five-coordinated Al atoms and bridged by two μ-hydroxo ligands. Alcohol exchange of **2** with Bu^nOH gave $[Al_5(\mu_5\text{-}O)(\mu\text{-}OBu^i)_8(OBu^i)_4(OBu^n)]$ **4** and of **1** with CF_3CH_2OH gave $[Al_4(\mu_4\text{-}O)(OBu^i)_6(OCH_2CF_3)_4(CF_3CH_2OH)]$ **6**. Other compounds synthesised were $[Al_4(OCH_2CF_3)_{12}]$ **7**, $[Al_4(\mu_4\text{-}O)(OCH_2CF_3)_{10}(CF_3CH_2OH)]$ **8**, $[Al\{OCH(CF_3)_2\}_3(THF)]$ **9**, and $[Al\{OCH(CF_3)_2\}_3(Et_2O)]$ **10**. Using ^{17}O enriched (10%) water, samples of **1**–**4**, **6** and **8** labelled at the oxo atom were prepared and their ^{17}O chemical shifts measured in addition to ^{1}H and ^{27}Al NMR chemical shifts. Possible reaction pathways for the formation of **2** and **3** from **1** are discussed. Structural aspects of aluminium oxoalkoxides are discussed.

Introduction

Metal oxoalkoxides are of current interest as intermediates in the conversion of metal alkoxide precursors into metal oxides using MOCVD or sol–gel techniques.[1] Only a few aluminium oxoalkoxides have hitherto been isolated and structurally characterised.[2] The first such compound reported was the remarkable decanuclear species $[Al_{10}O_4(OEt)_{22}]$ **5** which contains four-, five- and six-coordinated Al, obtained from aluminium ethoxide.[3] Recently the tetranuclear species $[Al_4(\mu_4\text{-}O)(OBu^i)_{10}(Bu^iOH)]$ **1** was obtained serendipitously by partial hydrolysis of $[Al_4(OBu^s)_{12}]$ in excess isobutanol solution and its X-ray structure showed the presence of five-coordinated Al.[4] Moreover, the isobutanol molecule was coordinated to one Al and hydrogen-bonded through the OH proton to a terminal isobutoxide group on an adjacent aluminium atom. It seemed reasonable to suppose that removal of the isobutanol molecule would cause closure of the structure to give a tetrahedral species $[Al_4(\mu_4\text{-}O)(\mu\text{-}OBu^i)_6(OBu^i)_4]$, but in attempting to do so we have isolated two novel oxoalkoxide species, one pentanuclear and the other octanuclear. In explaining these reactions we have prepared a number of other related compounds and attempted to elucidate reaction pathways using ^{17}O- and ^{27}Al-NMR spectroscopy.

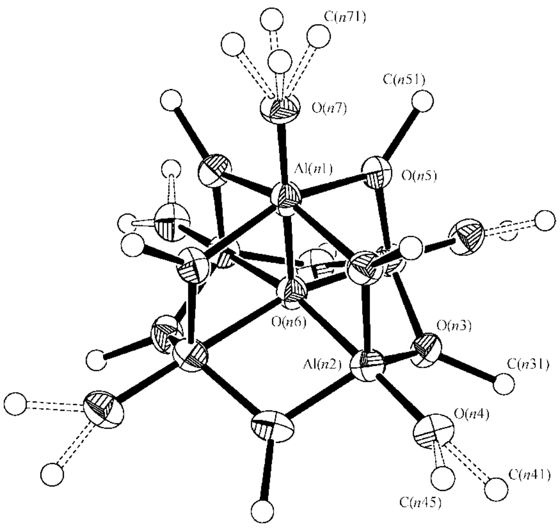

Fig. 1 Core structure of **2** showing thermal ellipsoids (30% probability) for Al and O atoms and spheres for C. Hydrogen and Pr^i carbon atoms are omitted for clarity. Disorder is illustrated by dashed bonds. General labelling scheme is shown with *n* representing the independent molecule number. Atomic positions correspond to molecule 2. C(*n*41/*n*45) disorder is not present in molecule 1.

Results and discussion

Treatment of **1** with DBU in boiling toluene gave two products, the crystalline $[Al_5(\mu_5\text{-}O)(\mu\text{-}OBu^i)_8(OBu^i)_5]$ **2** and an intractable oil containing aluminium oxo isobutoxide species together with DBU. The single crystal X-ray structure of **2** revealed (Fig. 1) that the μ_5-oxo atom is bonded to one apical six-coordinated aluminium and four basal five-coordinated aluminium atoms. Each Al has one terminal isobutoxo ligand and the structure is buttressed by eight bridging butoxo ligands spanning the edges of a square based pyramid. This structure is clearly related to that of the pentanuclear metal oxoisopropoxides $[M_5(\mu_5\text{-}O)(\mu_3\text{-}OPr^i)_4(\mu OPr^i)_4(OPr^i)_5]$ (M = Sc,[5] Y,[5,6] In,[5] Yb,[5] La,[7] Pr,[7] Sm,[7] Eu,[7] Er[7] and Lu[7]) in which the apical metal is μ_3-alkoxo bridged to the four basal metals giving each metal a distorted octahedral configuration.

An alternative approach to the removal of isobutanol from **1** entailed prolonged azeotropic fractional distillation of a toluene solution. A mixture of two products was obtained, the

DOI: 10.1039/b105876m

crystalline octanuclear species $[\mathrm{Al}_8(\mu_4\text{-O})_2(\mu\text{-OH})_2(\mu\text{-OBu}^i)_{10}(\mathrm{OBu}^i)_8]$ **3** and the more soluble $[\mathrm{Al}_4(\mathrm{OBu}^i)_{12}]$. The single crystal X-ray structure of **3** (Fig. 2) showed that the centrosymmetrical molecule is composed of two tetranuclear fragments bridged by two μ-hydroxo ligands and that each Al is five-coordinated as in the precursor molecule **1**. Compound **3** is thus a more hydrolysed species apparently obtained by disproportionation (eqn. 1).

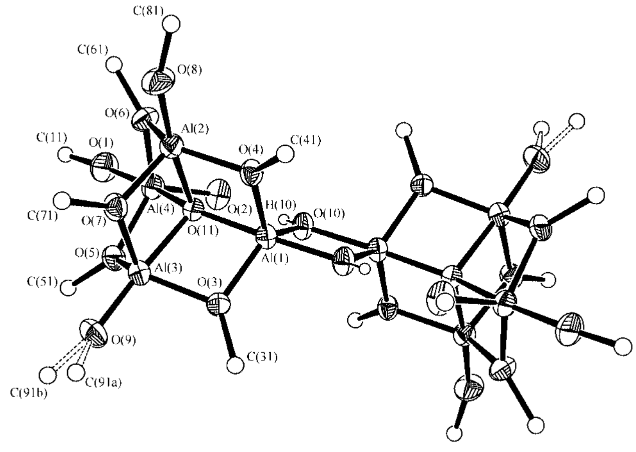

Fig. 2 Core structure of **3** showing thermal ellipsoids (30% probability) for Al and O atoms and spheres for C and H. Only μ-OH hydrogen atoms are shown, other hydrogen and Pr^i carbon atoms are omitted for clarity. Disorder is illustrated by dashed bonds.

$$4[\mathrm{Al}_4(\mu_4\text{-O})(\mathrm{OBu}^i)_{10}(\mathrm{Bu}^i\mathrm{OH})]\ \mathbf{1} \longrightarrow [\mathrm{Al}_8\mathrm{O}_2(\mathrm{OH})_2(\mathrm{OBu}^i)_{18}]\ \mathbf{3} + 2[\mathrm{Al}_4(\mathrm{OBu}^i)_{12}] + 2\mathrm{Bu}^i\mathrm{OH} \quad (1)$$

It is noteworthy that the decanuclear species $[\mathrm{Al}_{10}\mathrm{O}_4(\mathrm{OEt})_{22}]$ **5**[3] is also a dimer having two pentanuclear fragments linked by two μ_3-oxo bridges.

Treatment of the pentanuclear species **2** with *n*-butanol gave $[\mathrm{Al}_5(\mu_5\text{-O})(\mu\text{-OBu}^i)_8(\mathrm{OBu}^i)_4(\mathrm{OBu}^n)]$ **4** in which a preliminary X-ray structural determination shows that the terminal isobutoxo ligand on the apical Al has been replaced by a *n*-butoxide. Treatment of **1** with $\mathrm{CF_3CH_2OH}$ gave $[\mathrm{Al}_4(\mu_4\text{-O})(\mathrm{OBu}^i)_6(\mathrm{OCH_2CF_3})_4(\mathrm{CF_3CH_2OH})]$ **6** in which the tetranuclear framework has been retained. The tetranuclear compound $[\mathrm{Al}_4(\mu_4\text{-O})(\mathrm{OCH_2CF_3})_{10}(\mathrm{CF_3CH_2OH})]$ **8** was first reported by Sangokoya *et al*[8] as resulting from the reaction involving $\mathrm{Al_2Me_6}$ and trifluoroethanol. We have obtained **8** directly by controlled hydrolysis of $[\mathrm{Al}_4(\mathrm{OCH_2CF_3})_{12}]$ **7** which in turn was prepared directly from the reaction of Al metal with $\mathrm{CF_3CH_2OH}$. We have also obtained $[\mathrm{Al}\{\mathrm{OCH(CF_3)_2}\}_3(\mathrm{THF})]$ **9** and $[\mathrm{Al}\{\mathrm{OCH(CF_3)_2}\}_3(\mathrm{Et_2O})]$ **10** by direct reaction of Al metal with $\mathrm{(CF_3)_2CHOH}$ in the presence of THF and $\mathrm{Et_2O}$ respectively. Both **9** and **10** are volatile compounds, which were shown by mass spectra to retain their donor ligands in the vapour state.

^{17}O-NMR Spectra

In order to reveal aspects of the reaction pathways in the formation of compounds **2** and **3** we have used ^{17}O enriched (10%) water to prepare the oxo-labelled* compounds **1***, **2***, **3***, **4***, **6*** and **8*** for ^{17}O-NMR studies. Since compound **10** is a liquid its ^{17}O spectrum was obtained at natural abundance along with the spectra of $[\mathrm{Al}(\mathrm{OBu}^s)_{12}]$ and the alcohols $\mathrm{Bu}^i\mathrm{OH}$, $\mathrm{CF_3CH_2OH}$ and $\mathrm{(CF_3)_2CHOH}$. The ^{17}O-NMR data is listed in Table 1 and shows that for these types of molecules the chemical shifts fall into distinct regions, *viz.* μ_5-O, 90–95; μ_4-O, 80–86; μ_3-O, 7–47; μ_2-O, −30–0 ppm and are useful for diagnostic purposes. Similarly the ^{27}Al-NMR data (Table 2) proved useful in determining Al-coordination for structural assignments.

The formation of $[\mathrm{Al}_5\mathrm{O}(\mathrm{OBu}^i)_{13}]$ 2 from $[\mathrm{Al}_4\mathrm{O}(\mathrm{OBu}^i)_{10}(\mathrm{Bu}^i\mathrm{OH})]$ 1

Since the degree of hydrolysis, as measured by the ratio of oxo atoms to aluminium atoms, in compound **2** is lower than in compound **1** it follows that the other product of the reaction, an oil, should have a higher degree of hydrolysis. Examination of this oil showed that it contained DBU combined with aluminium isobutoxide. Its ^{17}O spectrum gave a large peak at 39.5 and a smaller one at 27.3 ppm. The presence of tetrahedral Al (^{27}Al, 67.9 ppm) and the fact that the DBU ^{1}H spectra were considerably shifted from free DBU, suggested the species $(\mathrm{DBUH})^+[\mathrm{Al}(\mathrm{OBu}^i)_4]^-$ and $[\mathrm{Al}(\mathrm{OBu}^i)_3(\mathrm{DBU})]$ as likely candidates. These compounds might be formed by degrading the tetranuclear species **1** to either or both of the trinuclear species **11** and **12** depicted in eqns 2 and 3. The proposed species **11** involves five-coordinated Al and a μ_3-O atom, which could be responsible for the ^{17}O signals at either 39.5 or 27.3 ppm. Species **12** involves four-coordinated Al and a three-coordinated oxygen in the μ-OH group (δ_O, 39.5 or 27.3 ppm). Both **11** and **12** have a much higher degree of hydrolysis than **1**. It remains to be explained how $[\mathrm{Al}_5(\mu_5\text{-O})(\mathrm{OBu}^i)_{13}]$ **2** becomes formed in this system. Compound **11** seems to offer a feasible route since it needs only to extract two $\mathrm{Al}(\mathrm{OBu}^i)_3$ fragments from say $[\mathrm{Al}(\mathrm{OBu}^i)_3(\mathrm{DBU})]$ to realise the pentanuclear product **2** as in eqn. 4. It is thus apparent from eqns. 2 and 4 how the labelled μ_4-O* in compound **1** can be transferred to the labelled μ_5-O* in the product **2**, which being the least soluble species crystallises out and is therefore isolated from the mixture.

$$[\mathrm{Al}_4\mathrm{O}^*(\mathrm{OBu}^i)_{10}(\mathrm{Bu}^i\mathrm{OH})]\ \mathbf{1} \xrightarrow{\mathrm{DBU}} [\mathrm{Al}_3(\mu_3\text{-O}^*)(\mu_3\text{-OBu}^i)(\mu\text{-OBu}^i)_3(\mathrm{OBu}^i)_3]\ \mathbf{11} + (\mathrm{DBUH})^+[\mathrm{Al}(\mathrm{OBu}^i)_4] \quad (2)$$

$$[\mathrm{Al}_4\mathrm{O}^*(\mathrm{OBu}^i)_{10}(\mathrm{Bu}^i\mathrm{OH})]\ \mathbf{1} \xrightarrow{\mathrm{DBU}} [\mathrm{Al}_3(\mu\text{-O}^*\mathrm{H})(\mu\text{-OBu}^i)_2(\mathrm{OBu}^i)_6]\ \mathbf{12} + [\mathrm{Al}(\mathrm{OBu}^i)_3(\mathrm{DBU})] \quad (3)$$

$$[\mathrm{Al}_3(\mu_3\text{-O}^*)(\mu_3\text{-OBu}^i)(\mu\text{-OBu}^i)_3(\mathrm{OBu}^i)_3] + 2[\mathrm{Al}(\mathrm{OBu}^i)_3(\mathrm{DBU})] \longrightarrow [\mathrm{Al}_5(\mu_5\text{-O}^*)(\mathrm{OBu}^i)_{13}]\ \mathbf{2} + 2\mathrm{DBU} \quad (4)$$

The formation of $[\mathrm{Al}_8\mathrm{O}_2(\mathrm{OH})_2(\mathrm{OBu}^i)_{18}]$ 3 from $[\mathrm{Al}_4\mathrm{O}(\mathrm{OBu}^i)_{10}(\mathrm{Bu}^i\mathrm{OH})]$ 1

The octanuclear compound **3** was obtained by subjecting a boiling toluene solution of **1** to azeotropic distillation to eliminate isobutanol. A plausible route to the reaction depicted in eqn. 1 would be *via* a combination of compounds **11** and **12** from eqns 2 and 3 with elimination of two $\mathrm{Al}(\mathrm{OBu}^i)_3$ units in the form of $[\mathrm{Al}_4(\mathrm{OBu}^i)_{12}]$ as depicted in eqn. 5. The tetranuclear species **13** thus produced dimerises to form the crystalline product **3**, eqn. 6.

$$[\mathrm{Al}_3\mathrm{O}^*(\mathrm{OBu}^i)_7]\ \mathbf{11} + [\mathrm{Al}_3(\mathrm{O}^*\mathrm{H})(\mathrm{OBu}^i)_8]\ \mathbf{12} \longrightarrow [\mathrm{Al}_4(\mu_4\text{-O}^*)(\mu\text{-OBu}^i)_6(\mathrm{OBu}^i)_3(\mathrm{O}^*\mathrm{H})]\ \mathbf{13} + \tfrac{1}{2}[\mathrm{Al}_4(\mathrm{OBu}^i)_{12}] \quad (5)$$

$$2[\mathrm{Al}_4(\mu_4\text{-O}^*)(\mathrm{OBu}^i)_9(\mathrm{O}^*\mathrm{H})]\ \mathbf{13} \longrightarrow [\mathrm{Al}_8(\mu_4\text{-O}^*)_2(\mu\text{-O}^*\mathrm{H})_2(\mathrm{OBu}^i)_{18}]\ \mathbf{3} \quad (6)$$

The presence of $[\mathrm{Al}_4(\mathrm{OBu}^i)_{12}]$ as depicted in eqn 1 was confirmed by its ^{1}H and ^{27}Al NMR spectra. The sequence of reactions shown in eqns. 2, 3, 5 and 6 offers a pathway for the labelled μ_4-O* in compound **1** to be transferred to the crystalline product **3** which contains μ_4-O* and μ-O*H. In the case of dealcoholation of compound **8** using DBU there was unfortunately no crystalline product, only an intractable oil.

Table 1 ^{17}O-NMR Data [a]

Compound	δ ^{17}O	Assignments
$[Al_5(\mu_5\text{-}O^*)(OBu^i)_{13}]$ **2**	91.75	Five-coordinated μ_5-O
$[Al_5(\mu_5\text{-}O^*)(OBu^i)_{12}(OBu^n)]$ **4**	93.65	Five-coordinated μ_5-O
$[Al_4(\mu_4\text{-}O^*)(OBu^i)_{10}(Bu^iOH)]$ **1**	82.15	Four-coordinated μ_4-O
$[Al_4(\mu_4\text{-}O^*)(OBu^i)_6(OCH_2CF_3)_5(H)]$ **6**	80.64	Four-coordinated μ_4-O
$[Al_4(\mu_4\text{-}O^*)(OCH_2CF_3)_{10}(CF_3CH_2OH)]$ **8**	85.89	Four-coordinated μ_4-O
$[Al_8(\mu_4\text{-}O^*)_2(O^*H)_2(OBu^i)_{18}]$ **3**	86.49	Four-coordinated μ_4-O
	27.84	Three-coordinated μ-OH
$[Al(OBu^s)_3]_n$	47.5	Three-coordinated μ-OBu^{sec}
$[Al_4\{OCH(CF_3)_2\}_3(Et_2O)]$ **10**	7.45	Three-coordinated $Et_2O \longrightarrow Al$
	−21.40	Two-coordinated Al–O–C
CF_3CH_2OH	−25.45	Two-coordinated H–O–C
$(CF_3)_2CHOH$	−11.04	Two-coordinated H–O–C
Bu^iOH	−2.92	Two-coordinated H–O–C

[a] O* enriched (10% ^{17}O) in solution in C_7D_8, all others as neat liquids natural abundance. Chemical shifts in ppm relative to D_2O.

Table 2 ^{27}Al-NMR Data [a]

Compound	Four-coord.	Five-coord.	Six-coord	T/K
$[Al\{OCH(CF_3)_2\}_3(Et_2O)]$ **10**	52.44 (*1*)			338
$[Al(\mu\text{-}OBu^i)_6\{Al(OBu^i)_2\}_3]$	65 (br) (*3*)		5.0 (*1*)	343
$[Al(\mu\text{-}OCH_2CF_3)_6\{Al(OCH_2CF_3)_2\}_3]$ **7**	60 (3) (*3*)		4.23 (*1*)	338
$[Al_4(\mu_4\text{-}O)(\mu\text{-}OBu^i)_5(OBu^i)_5(Bu^iOH)]$ **1**		34.7 (*4*)		343
$[Al_4(\mu_4\text{-}O)(OBu^i)_6(OCH_2CF_3)_4(CF_3CH_2OH)]$ **6**		32.65 (*4*)		337
$[Al_5(\mu_5\text{-}O)(\mu\text{-}OBu^i)_8(OBu^i)_5]$ **2**		32.31 (*4*)	5.0 (*1*)	337
$[Al_5(\mu_5\text{-}O)(\mu\text{-}OBu^i)_{12}(OBu^n)]$ **4**		33.31 (*4*)	5.0 (*1*)	337
$[Al_8(\mu_4\text{-}O)_2(\mu\text{-}OH)_2(\mu\text{-}OBu^i)_{10}(OBu^i)_8]$ **3**		39.1 (*8*)		343

[a] Chemical shifts in ppm relative to $Al_2(SO_4)_3$ aqueous solution. Solvent C_7D_8. Values in parentheses are relative number of Al atoms.

Nevertheless, the ^{17}O-NMR spectrum of this oil gave peaks at 26.7 and 18.9 ppm suggesting the presence of three-coordinated oxygen as perhaps in species such as $[Al_3(\mu_3\text{-}O^*)(OCH_2CF_3)_7]$ and $[Al_3(\mu\text{-}O^*H)(OCH_2CF_3)_8]$ the analogues of **11** and **12**.

Controlled hydrolysis of $[Al_4(OBu^i)_{12}]$

Compound **1** $[Al_4(\mu_4\text{-}O^*)(OBu^i)_{10}(Bu^iOH)]$ was readily obtained by addition of the requisite proportion of water in isobutanol to a solution of $[Al_4(OBu^i)_{12}]$, eqn. 7. Unfortunately it was not possible to obtain any characterisable compounds resulting from further hydrolysis although attempts were made to synthesise the oxoalkoxides **2**, **3** and the isobutoxide analogue of **5**. Instead gel-like materials were produced by increasing the degree of hydrolysis and their complex NMR spectra (^1H, ^{17}O and ^{27}Al) suggested the formation of polymeric materials. The ^{17}O spectra showed the presence of several μ_4-O* environments (δ_O, 70–81 ppm) together with a very broad peak at 44.6 ppm due to three-coordinated oxygen *e.g.* μ_3-O* and/or $Al_2(O^*H)$ groups.

$$H_2O^* + [Al_4(OBu^i)_{12}] \longrightarrow [Al_4(\mu_4\text{-}O^*)(OBu^i)_{10}(Bu^iOH)] + Bu^iOH \quad (7)$$

X-Ray crystal structure of $[Al_5(\mu_5\text{-}O)(\mu\text{-}OBu^i)_8(OBu^i)_5]$ 2 [9]

The structure of **2** is shown in Fig. 1 and some bond lengths and angles are collected in Table 3. As already mentioned, the molecular unit is based on an Al_5O_{14} framework containing one (apical) distorted octahedral Al, Al(*n*1), and four (basal) distorted trigonal bipyramidal Al atoms, Al(*n*2). It is noteworthy that the apical μ_5O–Al bond (O(*n*6)–Al(*n*1), av. 1.89 Å) is significantly shorter than the basal μ_5O–Al bonds (O(*n*6)–Al(*n*2), av. 2.08 Å) contrary to expectations and this causes the distortion of the tetragonal pyramid with the μ_5-oxo atom, O(*n*6), being displaced above the basal plane of four aluminiums. This is manifested in the Al(basal)–μ_5O–Al(apical) bond angles exceeding 90° (Al(*n*2)–O(*n*6)–Al(*n*1), av. 98°) and the *trans*-Al(basal)–μ_5O–Al(basal) angles being less than 180° (Al(*n*2)–O(*n*6)–Al(*n*2)″, av. 165°). Further evidence of distortion is shown in the longer bridging μO(R)–Al(apical) bonds (O(*n*5)–Al(*n*1), av. 1.96 Å). On the other hand the terminal O(R)–Al bonds are almost the same (O(*n*7)–Al(*n*1), 1.73 Å, apical; O(*n*4)–Al(*n*2), 1.72 Å, basal). Widening of the angle at M–O–C in terminal alkoxo metal systems is usually taken to reflect oxygen to metal π-electron donation so it is interesting to note that the angles are on average slightly wider for the basal aluminiums (Al(*n*2)–O(*n*4)–C(*n*41/5), av. 156°) than for the apical aluminiums (Al(*n*1)–O(*n*7)–C(*n*71), av. 154°). It is interesting to speculate why aluminium adopts this structure in preference to the alternative structure exhibited by the other tervalent pentanuclear metal oxo-*iso*propoxides,[5–7] which contain only octahedrally coordinated metals. It appears that the small size of the aluminium atom precludes the formation of the all-octahedral structure for steric reasons. Nevertheless, the related molecule $[H_5Al_5(\mu_5\text{-}O)(\mu\text{-}OBu^i)_8]$,[10] in which the terminal isobutoxo ligands of **2** are replaced by the small hydrido ligands, has virtually the same structure as **2** with similar Al–O bond distances and Al–O–Al bond angles. It is relevant to point out that the Al_4O_8 framework of the tetranuclear μ_4-oxo complex $[Al_4(\mu_4\text{-}O)(\mu\text{-}OBu^i)_5(OBu^i)_5(Bu^iOH)]$ **1** is also exhibited by the related molecule $[Al_4(\mu_4\text{-}O)(\mu\text{-}OCH_2CF_3)_5(OCH_2CF_3)_5(CF_3CH_2OH)]$ **8**[8] and the oxochloride isopropoxide $[Al_4(\mu_4\text{-}O)(\mu\text{-}OPr^i)_5(OPr^i)(Pr^iOH)Cl_4]$[11] in which the chlorides occupy terminal positions.

X-Ray crystal structure of $[Al_8(\mu_4\text{-}O)_2(\mu\text{-}OH)_2(\mu\text{-}OBu^i)_{10}(OBu^i)_8]$ 3

The octanuclear species **3** is a centrosymmetrical molecule comprising two tetranuclear units joined by two μ-OH ligands (Fig. 2). Some bond length and bond angle data are presented in Table 4. All of the aluminiums are in distorted trigonal bipyramidal configurations with Al(1) having no terminal isobutoxo ligands. Aluminiums (2), (3) and (4) each have one terminal alkoxo ligand *trans* to the μ_4-oxo defining the axial positions (O–Al–O angles 173.7, 176.9 and 166.4°) whilst Al(1) has one

Table 3 Some bond lengths (Å) and angles (°) in $[Al_5(\mu_5\text{-}O)(\mu\text{-}OBu^i)_8(OBu^i)_5]$ **2** with estimated standard deviations given in parentheses

		Molecule (*n*)[a]		
		n = 1	*n* = 2	Av.
O–Al				
	μ_5O–Al			
	O(*n*6)–Al(*n*1)	1.890(4)	1.880(5)	1.89
	O(*n*6)–Al(*n*2)	2.080(1)	2.087(1)	2.08
	μRO–Al			
	O(*n*3)–Al(*n*2)	1.832(2)	1.808(3)	1.82
	O(*n*3)′–Al(*n*2)	1.828(2)	1.830(3)	1.83
	O(*n*5)–Al(*n*2)	1.797(3)	1.801(3)	1.80
	O(*n*5)–Al(*n*1)	1.945(2)	1.969(2)	1.96
	RO(terminal)–Al			
	O(*n*4)–Al(*n*2)	1.722(2)	1.716(3)	1.72
	O(*n*7)–Al(*n*1)	1.734(6)	1.718(5)	1.73
O–Al–O				
	μRO–Al–μRO			
	O(*n*3)–Al(*n*2)–O(*n*3)′	122.6(2)	120.1(2)	121
	O(*n*3)–Al(*n*2)–O(*n*5)	110.4(1)	110.3(2)	110
	O(*n*3)′–Al(*n*2)–O(*n*5)	115.2(1)	116.8(1)	116
	O(*n*5)–Al(*n*1)–O(*n*5)′	87.99(3)	87.93(4)	88.0
	O(*n*5)–Al(*n*1)–O(*n*5)″	158.4(2)	158.1(2)	158
	μRO–Al–RO(terminal)			
	O(*n*3)–Al(*n*2)–O(*n*4)	102.3(1)	101.6(1)	102
	O(*n*3)′–Al(*n*2)–O(*n*4)	98.1(1)	101.3(1)	100
	O(*n*4)–Al(*n*2)–O(*n*5)	104.8(1)	103.6(1)	104
	O(*n*5)–Al(*n*1)–O(*n*7)	100.79(9)	101.0(1)	101
	μRO–Al–μ_5O			
	O(*n*3)–Al(*n*2)–O(*n*6)	77.62(9)	78.1(1)	78
	O(*n*3)′–Al(*n*2)–O(*n*6)	78.70(9)	77.7(1)	78
	O(*n*5)–Al(*n*2)–O(*n*6)	77.8(1)	77.8(1)	78
	O(*n*5)–Al(*n*1)–O(*n*6)	79.21(9)	79.1(1)	79
	RO(terminal)–Al–μ_5O			
	O(*n*4)–Al(*n*2)–O(*n*6)	176.5(1)	178.6(2)	178
	O(*n*7)–Al(*n*1)–O(*n*6)	180.0	180.0	180.0
Al–O–Al				
	Al–μRO–Al			
	Al(*n*2)–O(*n*3)–Al(*n*2)′	105.7(1)	106.9(1)	106
	Al(*n*2)–O(*n*5)–Al(*n*1)	105.6(1)	105.1(1)	105
	Al–μ_5O–Al			
	Al(*n*2)–O(*n*6)–Al(*n*2)′	89.09(3)	89.92(4)	89.5
	Al(*n*2)–O(*n*6)–Al(*n*2)″	165.5(2)	164.2(3)	165
	Al(*n*2)–O(*n*6)–Al(*n*1)	97.3(1)	97.9(1)	98
Al–O–C				
	Al–μO–C			
	Al(*n*2)–O(*n*3)–C(*n*31)	126.3(2)	125.3(3)	126
	Al(*n*2)′–O(*n*3)–C(*n*31)	124.1(2)	123.3(2)	124
	Al(*n*2)–O(*n*5)–C(*n*51)	125.4(2)	126.6(2)	126
	Al(*n*1)–O(*n*5)–C(*n*51)	128.9(2)	128.2(2)	129
	Al–O–C(terminal)			
	Al(*n*2)–O(*n*4)–C(*n*41)	165.2(2)	160.9(4)	156
	Al(22)–O(24)–C(245)		142.1(3)	
	Al(*n*1)–O(*n*7)–C(*n*71	156.2(5)	151.3(6)	154

[a] Independent molecules in each unit cell.

bridging hydroxyl ligand *trans* to the μ_4-oxo (173.1°). Aluminium (4) also has another terminal isobutoxo ligand O(2) which is hydrogen bonded to the proton of one of the bridging hydroxyls thus explaining the Al(4)–O(2) bond being significantly longer (1.766 Å). Each bridging isobutoxo ligand is unsymmetrically bonded to two aluminiums (shorter Al–O average 1.82 Å; longer Al–O average 1.87 Å). The hydroxo bridges to Al(1) are also unsymmetrical, with the shorter Al–O bond (1.790 Å *c.f.* 1.813 Å being *trans* to the μ_4-oxo ligand. The distortions in the trigonal bipyramids are evident in the values of the O–Al–O angles, with the axial ligands departing from 180° [Al(1), 173.1; Al(2), 173.7; Al(3), 176.9; Al(4), 166.4°], the *cis*-equatorial ligands deviating from 120° (averages, 119.3, 115.3, 115.5, 117.2°) and the *cis*-equatorial/axial ligands deviating from 90°, although the averages for each aluminium (90.1, 90.3, 90.1, 90.0°) are close to 90°. The configuration about the μ_4-oxo ligand is highly distorted tetrahedral (Al–O–Al, 98.6–145.1; average 108.1°) and it is clear that the structure of the tetranuclear precursor molecule **1** has been severely distorted during the conversion to the octanuclear species **3**.

Table 4 Some bond lengths (Å) and angles (°) in [$Al_8(\mu_4\text{-}O)_2(\mu\text{-}OH)_2(\mu\text{-}Bu^i)_{10}(OBu^i)_8$] **3** with estimated standard deviations given in parentheses

Al–O				
	µRO–Al		**RO(terminal)–Al**	
	O(3)–Al(1)	1.827(3)	O(1)–Al(4)	1.719(3)
	O(3)–Al(3)	1.868(3)	O(2)–Al(4)	1.766(3)
	O(4)–Al(1)	1.825(3)	O(8)–Al(2)	1.690(3)
	O(4)–Al(2)	1.766(3)	O(9)–Al(3)	1.695(4)
	O(5)–Al(3)	1.817(3)		
	O(5)–Al(4)	1.907(3)	**μ_4O–Al**	
	O(6)–Al(2)	1.845(3)	O(11)–Al(1)	1.816(3)
	O(6)–Al(4)	1.891(3)	O(11)–Al(2)	1.869(3)
	O(7)–Al(2)	1.833(3)	O(11)–Al(3)	1.914(3)
	O(7)–Al(3)	1.848(3)	O(11)–Al(4)	1.895(3)
	μ_2O–Al			
	O(10)–Al(1)	1.813(3)		
	O(10)′–Al(1)	1.790(4)		
O–Al–O				
	µRO–Al–µRO		**µRO–Al–µO**	
	O(3)–Al(1)–O(4)	110.9(1)	O(3)–Al(1)–O(10)	122.9(2)
	O(3)–Al(3)–O(5)	123.9(1)	O(3)–Al(1)–O(10)′	103.7(2)
	O(3)–Al(3)–O(7)	112.5(1)	O(4)–Al(1)–O(10)	124.1(2)
	O(4)–Al(2)–O(6)	134.1(1)	O(4)–Al(1)–O(10)′	103.3(2)
	O(4)–Al(2)–O(7)	104.3(3)		
	O(5)–Al(3)–O(7)	110.0(1)	**µRO–Al–μ_4O**	
	O(5)–Al(4)–O(6)	117.0(2)	O(3)–Al(1)–O(11)	80.5(1)
	O(6)–Al(2)–O(7)	107.5(2)	O(3)–Al(3)–O(11)	76.9(1)
			O(4)–Al(1)–O(11)	80.1(1)
	µRO–Al–RO(terminal)		O(4)–Al(2)–O(11)	77.0(1)
	O(3)–Al(3)–O(9)	100.1(2)	O(5)–Al(3)–O(11)	77.4(1)
	O(4)–Al(2)–O(8)	99.8(2)	O(5)–Al(4)–O(11)	75.7(1)
	O(5)–Al(3)–O(9)	104.1(1)	O(6)–Al(2)–O(11)	76.8(3)
	O(5)–Al(4)–O(1)	97.2(2)	O(6)–Al(4)–O(11)	75.1(1)
	O(5)–Al(4)–O(2)	117.2(2)	O(7)–Al(2)–O(11)	80.2(1)
	O(6)–Al(2)–O(8)	102.2(2)	O(7)–Al(3)–O(11)	78.7(1)
	O(6)–Al(4)–O(1)	98.6(2)		
	O(6)–Al(4)–O(2)	117.4(2)	**RO(terminal)–Al–RO(terminal)**	
	O(7)–Al(2)–O(8)	105.9(2)	O(1)–Al(4)–O(2)	103.5(2)
	O(7)–Al(3)–O(9)	103.2(2)		
	RO(Terminal)–Al–μ_4O		**μ_2O–Al–μ_2O**	
	O(1)–Al(4)–O(11)	166.4(2)	O(10)–Al(1)–O(10)′	79.4(2)
	O(2)–Al(4)–O(11)	90.1(1)		
	O(8)–Al(2)–O(11)	173.7(2)	**μ_2O–Al–μ_4O**	
	O(9)–Al(3)–O(11)	176.9(3)	O(10)–Al(1)–O(11)	93.7(2)
			O(10)′–Al(1)–O(11)	173.1(2)
Al–O–Al				
	Al–µOR–Al		**Al–μ_4O–Al**	
	Al(1)–O(3)–Al(3)	101.2(1)	Al(1)–O(11)–Al(2)	102.1(1)
	Al(1)–O(4)–Al(2)	100.8(1)	Al(1)–O(11)–Al(3)	99.8(1)
	Al(2)–O(6)–Al(4)	103.6(2)	Al(1)–O(11)–Al(4)	145.1(2)
	Al(2)–O(7)–Al(3)	103.4(1)	Al(2)–O(11)–Al(3)	98.6(1)
	Al(3)–O(5)–Al(4)	103.8(1)	Al(2)–O(11)–Al(4)	102.6(1)
			Al(3)–O(11)–Al(4)	100.6(1)
	Al–μ_2–Al			
	Al(1)–O(10)–Al(1)′	100.6(2)		
Al–O–C				
	Al–µO–C		**Al–O–C(terminal)**	
	Al(1)–O(3)–C(31)	130.1(3)	Al(2)–O(8)–C(81)	154.1(7)
	Al(1)–O(4)–C(41)	130.2(3)	Al(3)–O(9)–C(91a)	145.7(8)
	Al(2)–O(4)–C(41)	127.7(3)	Al(3)–O(9)–C(91b)	163.1(9)
	Al(2)–O(6)–C(61)	127.7(3)	Al(4)–O(1)–C(11)	170.8(8)
	Al(2)–O(7)–C(71)	126.8(3)	Al(4)–O(2)–C(21)	125.9(3)
	Al(3)–O(3)–C(31)	128.3(3)		
	Al(3)–O(5)–C(51)	127.1(3)		
	Al(3)–O(7)–C(71)	130.7(3)		
	Al(4)–O(5)–C(51)	128.2(3)		
	Al(4)–O(6)–C(61)	127.4(3)		

Structural aspects of aluminium oxoalkoxides

A notable feature of the structural chemistry of the aluminium oxoalkoxides **1**–**5**, **8** [$H_5Al_5O(OBu^i)_8$] and [$Cl_4AlO(OPr^i)_6(Pr^iOH)$] is the variety of coordination numbers (four, five and six) exhibited by the aluminium atoms. In the stable form of the tetranuclear parent aluminium alkoxides [$Al(\mu\text{-}OR)_6\{Al(OR)_2\}_3$] the central octahedrally coordinated Al is bridged by three tetrahedrally coordinated aluminiums.[12] In the tetranuclear μ_4-oxo centred species [$Al_4(\mu_4\text{-}O)(\mu\text{-}OR)_5(OR)_5(ROH)$] **1** all of the aluminiums are five-coordinated, but in the pentanuclear μ_5-oxo centred species [$Al_5(\mu_5\text{-}O)(\mu\text{-}OR)_8(OR)_5$] **2** there is one six-coordinated Al and four five-coordinated. The more hydrolysed octanuclear species [$Al_8(\mu_4\text{-}O)_2(\mu\text{-}OH)_2(\mu\text{-}OBu^i)_{10}$-

$(\text{OBu}^i)_8]$ **3** exhibits only five-coordinated metals whereas the decanuclear $[\text{Al}_{10}(\mu_4\text{-O})_2(\mu_3\text{-O})_2(\mu\text{-OEt})_{14}(\text{OEt})_8]$ **5** surprisingly has four-, five- and six- coordinated aluminiums. Since the decanuclear compound corresponds to $\text{AlO}_{0.4}(\text{OEt})_{2.2}$ in composition it is evident that further hydrolysis should lead to higher polymers. Complete hydrolysis leads to the formation of all six-coordinated Al in the oxide Al_2O_3. Many years ago we studied the controlled hydrolysis of several metal alkoxides and trialkylsilyloxides in their progenitive alcohols using ebulliometric measurements to determine the number average degree of polymerisation n as a function of the degree of hydrolysis h (ratio of H_2O : metal).[13] In most cases a linear relationship between n^{-1} and h was found and attempts were made to fit these results to possible structural models for the metal oxide alkoxides. In the case of aluminium it was found that the unhydrolysed aluminium isopropoxide was predominantly trimeric (n = 3.16) in boiling isopropanol and controlled hydrolysis up to h = 0.948 gave a linear plot of n^{-1} *vs.* h.[14] The values of n corresponding to h = 0.20, 0.25, 0.40 and 0.50 were respectively 4.08, 4.40, 5.78 and 7.30 compared with the values of the known crystalline aluminium oxide alkoxides of **2** (5.0), **1** (4.0), **5** (10.0) and **3** (8.0). Evidently the structural behaviour of aluminium oxide isopropoxides in boiling isopropanol solution does not correspond to any of the known crystal structures of the aluminium oxide isobutoxides reported in this research. The solution studies are complicated by possible solvation by the alcohol, as indeed found in the crystalline species $[\text{Al}_4(\mu_4\text{-O})(\mu\text{-OR})_5(\text{OR})_5(\text{ROH})]$, and also by the possibility that hydroxo species may be present, as found in the crystalline $[\text{Al}_8(\mu_4\text{-O})_2(\mu\text{-OH})_2(\mu\text{-OBu}^i)_{10}(\text{OBu}^i)_8]$. Although the use of ^{17}O and ^{27}Al NMR spectroscopy in the present study of the controlled hydrolysis of aluminium isobutoxide in isobutanol has given some information concerning the coordination of the aluminiums and oxo ligands in the more polymeric gel-like products, the inherently broad line spectra given by these quadrupolar nuclei has imposed severe limitations and other techniques, *e.g.* EXAFS and XANES might well prove more successful in characterising the more polymeric species. In conclusion we note the predominance of tetranuclear and pentanuclear oxo-centred units in the structures of crystalline aluminium oxoalkoxides.

Experimental

All manipulations were carried out under dry nitrogen using vacuum-line, glove box and Schlenk style apparatus.

NMR Spectra

Proton and ^{13}C NMR spectra were obtained using Bruker WM 250 and WH 400 FT spectrometers in C_6D_6 and C_7D_8 solutions and referenced to TMS. ^{19}F spectra were referenced to CFCl_3, ^{17}O spectra to D_2O and ^{27}Al spectra to $\text{Al}_2(\text{SO}_4)_3$ aqueous solution. Some ^{17}O spectra at natural abundance were obtained on neat liquid samples using the Bruker AMX 600 MHz spectrometer (University of London Intercollegiate Research Service, ULIRS).

Mass spectra were obtained using a Kratos MS50TC spectrometer (70 eV) and infrared spectra (Nujol mulls) in the 400–200 cm^{-1} range using a Perkin-Elmer FT 1720 spectrophotometer.

The C and H analyses were obtained commercially from either Butterworth Microanalytical Laboratories or University College London. The aluminium was determined gravimetrically on the macro scale.

Preparations

$[\text{Al}_4(\text{OBu}^i)_{12}]$. Commercial (Aldrich) aluminium tris-*sec*-butoxide was distilled (140 °C/10^{-2} Torr) and treated with excess Bu^iOH. The crystals deposited were recrystallised from Bu^iOH. The product (mp. 218–221 °C) sublimed unchanged at 200 °C/10^{-2} Torr. NMR: ^{1}H (C_6D_6): (4.04d, 4.02d, 3.88d, 3.85d; 12H, CH_2), (3.82d; 12H, CH_2); (2.15spt; 6H, CH); (1.85spt, 6H, CH; (1.14d, 1.13d; 36H, CH_3); (1.06d, 1.05d; 36H, CH_3). ^{13}C (C_6D_6); (72.68, 71.18; CH_2); (33.66, 31.58; CH); (20.73, 20.45, 20.25; CH_3). ^{27}Al (C_7D_8, 343 K); (65br, 3Al); (5.0, 1Al). IR: 2770w, 2723m, 1391s, 1364m 1273w, 1147s, 1029s, 947s, 912m, 829m, 802m, 780s, 736s, 623s, 536w, 486w, 430w, 411w cm^{-1}. Mass spectrum: *m/z* 911.4557 $[\text{Al}_4(\text{OBu})_{11}]^+$; 781.5054 $[\text{Al}_4\text{O}(\text{OBu})_9]^+$.

$[\text{Al}_4\text{O}(\text{OBu}^i)_{10}(\text{Bu}^i\text{OH})]$ 1. Aqueous Bu^iOH was added dropwise with stirring to a solution of $\text{Al}_4(\text{OBu}^i)_{12}$ in Bu^iOH (ratio H_2O to Al; 1 : 4) and set aside. Crystals of **1** (mp. 140–143 °C) deposited over several days. NMR: ^{1}H (C_6D_6): (3.92d, 3.89d, 3.88d, 3.85d, 3.76d, br; ratio 4 : 2 : 2 : 1 : 2, CH_2); (2.26spt, 2.11m, 1.95spt; CH); (1.15d, 1.14d, 1.12d, 1.11d, 1.10d, 1.02d; ratio 2 : 2 : 2 : 1 : 2 : 2; CH_3). ^{27}Al (C_7D_8, 343 K): 34.7. ^{17}O (C_7D_8, 337 K): 82.15 (half width 35 Hz), μ_4-O, from a sample enriched 10% in ^{17}O. IR: 2720m, 1392s, 1306w, 1283w, 1163s, 1125s, 1065s, 960m, 912m, 823m, 736s, 633s, 535m, 467w, 417w, 347w, 237w, 217w cm^{-1}.

$[\text{Al}_5\text{O}(\text{OBu}^i)_{13}]$ 2. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 2 cm^3,13 mmol) was added to a solution of **1** (5.83 g, 6 mmol) in toluene (120 cm^3) and left overnight. After refluxing for 1 h the solution was concentrated to *ca.* 30 cm^3 and cooled. The crystalline product was recrystallised twice from toluene to give **2** (3.6 g, mp. 219–223 °C). Found: C, 55.7; H, 10.7; Al 12.1. Calc. for $\text{Al}_5\text{O}(\text{OBu}^i)_{13}$: C, 56.7; H 10.6; Al 12.2%. NMR: ^{1}H (C_6D_6); (4.05d; 16H, CH_2); (3.94d; 10H, CH_2); (2.35spt; 8H, CH); (1.99spt; 5H, CH); (1.15d; 30H, CH_3); (1.17d; 48H, CH_3). ^{1}H (C_7D_8; 193 K): (4.24, 4.12, 3.99, 3.83; CH_2); (2.44, 2.30, 2.07; CH); (1.36sh; 1.32, 1.22, 1.08, 1.02; CH_3). ^{13}C (C_6D_6): (73.30, 71.15; CH_2); (33.87, 30.71; CH); (20.70, 20.01; CH_3). ^{27}Al (C_7D_8, 343 K); (32.31br, 4Al); (4.91, 1Al). ^{17}O (C_7D_8, 337 K); (91.75; μ_5-O, from sample enriched 10% in ^{17}O). IR: 1392m, 1272w, 1170s, 1125m, 1065s, 1038s, 959w, 946w, 910w, 824w, 693s, 605m, 497s, 443m, 345m, 229w, 222w cm^{-1}.

$[\text{Al}_8\text{O}_2(\text{OH})_2(\text{OBu}^i)_{18}]$ 3. Several hours of fractional distillation of a solution of **1** (3.84 g) in toluene (150 cm^3) was required to remove Bu^iOH. The residual solution (20 cm^3) was stripped of solvent *in vacuo* leaving a sticky residue, which gave ^{1}H NMR signals (C_7D_8) at δ 3.88m, 2.32spt, 1.94spt and 1.14d in addition to those due to $\text{Al}_4(\text{OBu}^i)_{12}$. The residue was redissolved in toluene and compound **3** obtained pure by several recrystallisations. NMR: ^{1}H (C_6D_6); (3.87m, CH_2); (2.32spt, 1.94spt; CH); (1.14m, CH_3). ^{27}Al (C_7D_8, 343 K): (39.10). ^{17}O (C_7D_8, 338 K): (86.49, half width 100 Hz); (27.84, half width 270 Hz).

$[\text{Al}_5\text{O}(\text{OBu}^i)_{12}(\text{OBu}^n)]$ 4. Bu^nOH (0.25 cm^3) was added to a solution of **2** (1.38 g) in toluene (20 cm^3) giving a molar ratio of Bu^nOH : $\text{Al}_5\text{O}(\text{Bu}^i)_{13}$ of 2 : 1. After standing overnight the solution was concentrated to *ca.* 1 cm^3 and on cooling to 4 °C deposited crystals of **4** (1.05 g, mp. 209–215 °C). Found: C, 55.1; H, 10.4. Calc. for $\text{Al}_5\text{O}(\text{OBu})_{13}$: C, 56.7; H, 10.6%. NMR: ^{1}H (C_6D_6): (4.20m, 4.04m, 3.93m; CH_2); (2.35m, 2.00m; CH); (1.45m; CH_2); (1.13m, 1.08m; CH_3). ^{27}Al (C_7D_8, 337K): (33.31br, 4Al); (5.00, 1Al). ^{17}O (C_7D_8, 337 K); (93.65, μ_5-O from sample enriched 10% in ^{17}O). IR: 1392s, 1366s, 1267m, 1180s, br, 1125s, 1069s,1040s, 960m, 946m, 910m, 858w, 823m, 804w, 671s, br, 506s, 443m, 345m, 222w, 217w cm^{-1}. Treatment of **1** with excess of Bu^nOH caused replacement of all OBu^i groups but the product was an intractable oil.

$[\text{Al}_4\text{O}(\text{OBu}^i)_6(\text{OCH}_2\text{CF}_3)_4(\text{CF}_3\text{CH}_2\text{OH})]$ 6. Trifluoroethanol (2.5 cm^3) was added to a solution of **1** (1.7 g) in toluene (40 cm^3) and left overnight. The solution was concentrated to small volume and cooled to cause crystallisation. NMR revealed the presence of both OBu^i and OCH$_2$CF$_3$ groups in the crystals which were redissolved in benzene and more CF$_3$CH$_2$OH (1 cm^3) added. After refluxing the solution for 1 h it was evaporated to dryness *in vacuo* and the residue was crystallised from toluene (1.2 g, mp. 218–224 °C). Found: C, 37.8; H, 6.1; Al 10.1; Calc. for Al$_4$O(OBu^i)$_6$(OCH$_2$CF$_3$)$_5$H: C, 38.6; H 6.2; Al, 10.2%. NMR: ^{1}H (C$_6$D$_6$): (4.19m; 10H, CH_2CF$_3$); (3.59m; 12H, CH_2CHMe$_2$); (1.92m; 6H CH$_2$CHMe$_2$); (0.93m, 0.85d; 36H, CH$_3$). ^{27}Al (C$_7$D$_8$, 337 K): 32.65. ^{17}O (C$_7$D$_8$, 337 K): (80.64, half width 34 Hz, μ$_4$-O from enriched sample). ^{19}F (C$_6$D$_6$): (−77.48m, 4F; −77.65, 1F). IR: 1419m, 1396m, 1300s, 1219s, 1163s, 1057s, 962s, 911m, 828m, 747s, 665s, 618s, 537m, 482w, 466w, 422m, 383w, 347m cm^{-1}.

[Al$_4$(OCH$_2$CF$_3$)$_{12}$] 7. Trifluoroethanol (10 cm^3) was added to aluminium turnings (0.5 g) and heated under reflux until all the Al had dissolved (*ca.* 2 h.) The solidified product was recrystallised from toluene (5.4 g, mp. 160–169 °C). Found: C, 21.6; H, 1.6; Al, 8.2. Calc. for Al(OCH$_2$CF$_3$)$_3$: C, 22.2; H 1.9; Al, 8.3%. NMR: ^{1}H (C$_6$D$_6$): (4.49m, 6H; 4.40m, 6H; 3.69q, 12H). ^{19}F (C$_6$D$_6$): (−76.44t, 18F; −78.87t, 18F). ^{27}Al (C$_7$D$_8$, 338 K): (60br, 3Al; 4.23, 1Al). IR: 1285s, 1162s, 1064s, 963s, 843m, 831m, 816m, 747w, 692m, 657m, 620m, 595s, 573w, 555w, 542m, 458w, 408m, 364w, 337w, 298w, 214w cm^{-1}. Mass spectrum, *m*/*z*: 789.0045, [Al$_3$(OCH$_2$CF$_3$)$_7$CH$_3$]$^+$, calc. 789.0085; 709.0051, [Al$_3$F(OCH$_2$CF$_3$)$_6$CH$_3$]$^+$, calc. 709.0021; 678.9642, [Al$_4$O(OCH$_2$CF$_3$)$_7$ − 2CF$_3$]$^+$, calc. 678.9711; 628.9817, [Al$_4$O(OCH$_2$CF$_3$)$_7$ − 2CF$_3$ − CF$_2$]$^+$, calc 628.9743. Compound **7** sublimed at 120 °C/10^{-2} Torr with some decomposition.

[Al$_4$(μ$_4$-O)(OCH$_2$CF$_3$)$_{10}$(CF$_3$CH$_2$OH)] 8. Water (0.04 cm^3) in trifluoroethanol (10 cm^3) was added dropwise to a solution of **7** (3.56 g) in CF$_3$CH$_2$OH (50 cm^3). Concentration of this solution caused the deposition of lustrous crystals (2.13 g, mp. 139–142 °C). Found: C, 20.7; H, 1.6; Al, 8.6. Calc. for Al$_4$O(OCH$_2$CF$_3$)$_{10}$CF$_3$CH$_2$OH: C, 21.8; H 1.9; Al, 8.9%. NMR ^{1}H (C$_6$D$_6$/C$_6$F$_6$ mixture): (9.5, OH); (4.53q, 4.43q, 4.41q, 4.25 br. q). IR: 1423m, 1285s, 1230s, 1163s, 1105s, 973s, 838m, 768m, 751s, 688s, 661s, 624s, 575m, 540m, 516m, 425m, 402w, 353m, 343w, 295w, 272w, 240w, 220w cm^{-1}. Compound **8** was sublimed at 110 °C/10^{-2} Torr (mp. 137–140 °C). ^{1}H NMR (C$_6$D$_6$/C$_6$F$_6$ mixture): (13.87, OH); (4.53 q, 4.43q, 4.41q). ^{19}F decoupled ^{1}H(C$_6$D$_6$/C$_6$F$_6$ mixture): (4.57; 4.54, 4.51, 4.43, 4.41, 4.39; ratio 1 : 1 : 1 : 3 : 4). ^{17}O (C$_6$D$_6$/C$_6$F$_6$ mixture, 1 : 5): 85.89, halfwidth 40 Hz; μ$_4$-O from 10% enriched ^{17}O).

[Al{OCH(CF$_3$)$_2$}$_3$(THF)] 9. Aluminium turnings (0.3 g) were refluxed with hexafluoro-isopropanol (5 cm^3) and THF (5 cm^3) in toluene (5 cm^3) until reaction was complete. After evaporation to dryness *in vacuo* the residue was dissolved in toluene (100 cm^3), filtered to remove impurities and the product (4.2 g, mp. 89–93 °C) obtained by crystallisation. Compound **9** sublimed at 90 °C/10^{-2} Torr. Found: C, 25.5; H, 1.7; Al, 4.7. Calc for Al{OCH(CF$_3$)$_2$}$_3$(THF): C, 26.0; H, 1.8; Al, 4.5%. NMR: ^{1}H (C$_6$D$_6$): (4.52spt, 3H, CH); (3.57m, 4H, THF); (0.89m, 4H, THF). IR: 1295s, 1181s, 1100s, 1045w, 995m, 959w, 918m, 894s, 856s, 824m, 773w, 729m, 716w, 687s, 572m, 551w, 536w, 521m, 503w, 436s, 330w, 292w, 278w, 228w, 223w cm^{-1}. Mass spectrum, *m*/*z*: 531.0437, [Al{OCH(CF$_3$)$_2$}$_3$(THF) − CF$_3$]$^+$, (calc. 531.0233); 433.0346, [Al{OCH(CF$_3$)$_2$}$_2$(THF)]$^+$, (calc. 433.0254); 285.0331, [AlF{OCH(CF$_3$)$_2$}(THF)]$^+$, (calc. 285.0306); 137.0392, [AlF$_2$(THF)]$^+$, (calc. 137.0358).

[Al{OCH(CF$_3$)$_2$}(Et$_2$O)] 10. Aluminium turnings (0.3 g) reacted vigorously with (CF$_3$)$_2$CHOH (5 cm^3) in diethyl ether (15 cm^3) after initiation with a catalytic amount of HgCl$_2$. After filtration the solvent was evaporated *in vacuo* and the residue distilled at 80 °C/10^{-2} Torr giving a clear liquid (5.2 g). Found: C, 25.7; H, 2.1; Al, 4.4%. Calc. for [Al{OCH(CF$_3$)$_2$}(Et$_2$O)]: C, 25.9; H, 2.2; Al, 4.5%. NMR: ^{1}H (C$_6$D$_6$); (4.50spt, 3H); (3.42q, 4H); (0.70br, 6H). 27Al (C$_7$D$_8$, 338 K): (52.44). ^{17}O (neat sample, 338 K): (7.45, half width 300 Hz, one O); (−21.40, half width 800 Hz, three O). IR (neat): 2997w, 2915w, 1474w, 1453w, 1378s, 1300s, 1191s, 1103s, 1009m, 894s, 856s, 822m, 778m, 729w, 688s, 571m, 536w, 522m, 437m cm^{-1}. Mass spectrum, *m*/*z*: 583.0326, [Al{OCH(CF$_3$)$_2$}$_3$(Et$_2$O) − F]$^+$, (calc. 583.0358); 533.0365, [Al{OCH(CF$_3$)$_2$}$_3$(Et$_2$O) − CF$_3$]$^+$, (calc. 533.0390); 435.0409, [Al{OCH(CF$_3$)$_2$}$_2$(Et$_2$O)]$^+$, (calc. 435.0410). 287.0473, [Al{OCH(CF$_3$)$_2$}F(Et$_2$O)]$^+$, (calc. 287.0463). 237.0468, [Al{OCH(CF$_3$)$_2$}(Et$_2$O) − CF$_3$]$^+$, (calc. 237.0494).

Hydrolysis investigations

Controlled hydrolysis of [Al$_4$(OBu^i)$_{12}$]. In preparing compound **1** by the hydrolysis of Al$_4$(OBu^i)$_{12}$ in Bu^{i}OH several experiments were carried out involving different molar ratios of H$_2$O : Al$_4$(OR)$_{12}$. With a low ratio (0.1 : 1.0) the hydrolysis appeared to be slow as judged by the delay (several days) in the appearance of crystals of **1**. With the optimum ratio (1 : 1) crystals deposited over a period of 24 h. Using ^{17}O enriched (10%) H$_2$O it was shown that the oxo-atom (δ_O 82.15 ppm) in **1** definitely originated from the water. Using higher ratios (3 : 1 to 7 : 1), the yield of **1** decreased and gel-like aluminium compounds were produced. The IR spectra of these gels showed a broad band around 3600 cm^{-1} increasing in intensity with increased degree of hydrolysis presumably due to Al–OH groups. Other strong broad bands were observed at 1078–1083 and 643 cm^{-1}. The ^{1}H NMR spectra gave several overlapping peaks due to OBu^i groups in various environments and becoming weaker with increasing degree of hydrolysis. The ^{27}Al spectra showed overlapping peaks for four-, five- and six- coordinated Al species, whilst the ^{17}O spectra showed decreasing intensities of the peak due to **1** (μ$_4$-O at 82.15 ppm) together with other μ$_4$-O species (δ_O 70–81 ppm) and a very broad peak at 44.6 indicative of μ$_3$-O presumably due to Al–OH–Al or Al$_3$O groups.

The oil produced by reaction of 1 with DBU. The reaction of **1** (μ$_4$-O enriched in ^{17}O) with DBU in refluxing toluene gave crystals of **2** and an oil. The ^{1}H NMR spectrum of this oil showed peaks due to OBu^i groups together with a complex pattern of shifted DBU peaks. Distillation of the oil at 90 °C/10^{-2} Torr gave a distillate comprising a mixture of DBU and Bu^{i}OH leaving a residue of [Al$_4$(OBu^i)$_{12}$]. The ^{27}Al spectrum of the oil gave a single peak at 67.9 ppm due to tetrahedrally coordinated Al whilst the ^{17}O spectrum gave a main broad peak at 39.5 ppm and a smaller one at 27.3 ppm, both of which are in the region for three-coordinated oxygen of μ-O or μ-OH. These data suggest that the oil is a mixture containing for example (DBUH)$^+$ [Al(OBu^i)$_4$]$^-$ or the adduct [Al(OBu^i)$_3$(DBU)] and one or more Al-containing species such as [Al$_3$(μ-OH)(μ-OBu^i)$_2$(OBu^i)$_6$] (see Discussion) or [Al$_3$(μ$_3$-O)(μ$_3$-OR)(μ-OR)$_3$(OR)$_3$]. Interestingly when [Al$_4$(OBu^i)$_{12}$], Bu^{i}OH and DBU in the molar ratio 1 : 4 : 4 were dissolved in toluene and the volatiles then removed, an oil remained which had ^{1}H NMR and IR spectra typical of the oil obtained from **1** and DBU.

The oil produced in the reaction of 8 with DBU. The reaction of [Al$_4$O(OCH$_2$CF$_3$)$_{10}$(CF$_3$CH$_2$OH)] **8** (containing μ$_4$-O enriched with ^{17}O) with DBU also produced an oil, but no crystalline product. The ^{1}H NMR spectrum of the oil gave peaks for OCH$_2$CF$_3$ and DBU in a 4 : 1 molar ratio, the ^{27}Al spectrum gave one peak at 66.3 ppm due to tetrahedral Al and the ^{17}O spectrum gave peaks at 26.7 and 18.9 ppm suggesting the presence of three-coordinated oxygen, *e.g.* μ$_3$-O in an Al$_3$O group or Al$_2$(OH).

Table 5 Crystal data and structure refinement for $[Al_5(\mu_5\text{-}O)(\mu\text{-}OBu^i)_8(OBu^i)_5]$ **2**, $[Al_8(\mu_4\text{-}O)_2(\mu\text{-}OH)_2(\mu\text{-}OBu^i)_{10}(OBu^i)_8]$ **3**

Compound	**2**	**3**
Formula	$C_{52}H_{117}Al_5O_{14}$	$C_{72}H_{164}Al_8O_{22}$
M	1101.36	1597.87
T/K	150(2)	293(2)
Crystal system	Tetragonal	Monoclinic
Space group	$P4cc$	$C2/c$
Cell dimensions	a = 13.493(1) Å c = 36.699(4) Å	a = 29.882(5) Å b = 19.276(8) Å c = 18.192(4) Å β = 99.81(3)°
U/Å^3	6682(1)	10118(5)
Z	4	4
μ (MoK_α)/mm^{-1}	0.136	0.137
Reflections collected	29967	9062
Independent reflections	6834	8876
R_{int}	0.0713	0.0329
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0565$, $wR_2 = 0.1265$	$R_1 = 0.0624$, $wR_2 = 0.1517$
R indices (all data)	$R_1 = 0.0734$, $wR_2 = 0.1335$	$R_1 = 0.1997$, $wR_2 = 0.2009$

X-Ray crystal structures of 2 and 3

Single crystals of both compounds were grown from toluene solutions. Summaries of data collection and structure refinement are given in Table 5. The intensity data for **2** were collected using a FAST area detector at 150(2) K. Data collection, reduction and cell refinement procedures are described elsewhere.[15] An absorption correction was carried out on unmerged data with the refined isotropic model using the program DIFABS.[16] Intensity data for **3** were collected on an Enraf Nonius CAD-4 diffractometer using MoKα radiation (λ = 0.71069 Å) with ω–2θ scans at 293(2) K. All data were corrected for absorption by empirical methods (ψ-scan).[17] Both structures were solved by direct methods using the SHELXS-97 programme[18] and refined on F^2 using the SHELXL-97 programme.[18] Anisotropic parameters were refined for all non-hydrogen atoms. The H atoms were calculated geometrically and refined with a riding model.

The structure of **2** crystallises in a tetragonal cell. Systematic absences in the data were somewhat ambiguous and several solutions in various tetragonal space groups were possible. A space group of $P4$ was chosen for the initial solution. However it was apparent that while the Al_5O_{14} cores do indeed show tetragonal symmetry ($P4cc$), the apical isobutoxy ligand necessitates a lowering of the symmetry to triclinic $P1$. Isotropic refinement of the core atoms in the triclinic space group was possible, but further refinement was hindered by the large number of variable parameters in this space group. The model presented here represents the averaged situation in the tetragonal space group $P4cc$. Contact distance restraints were required in several of the isobutoxy ligands. In the case of **3** disorder in some of the isobutoxy ligands was modelled by splitting sites and refining using equal fixed occupancies. Molecular graphics were obtained using ORTEP3 for Windows.[19]

CCDC reference numbers 173335 and 173336.

See http://www.rsc.org/suppdata/dt/b1/b105876m/ for crystallographic data in CIF or other electronic format.

Acknowledgements

This research was partly supported by a 3M Leading Edge Academic Program grant. We thank Greg Coumbarides for obtaining the NMR spectra and Peter Cook for the mass spectra.

References

1 L. G. Hubert-Pfalzgraf, *New. J. Chem.*, 1987, **11**, 63; D. C. Bradley, *Chem. Rev.*, 1989, **89**, 1317.
2 R. C. Mehrotra and Anirudh Singh, *Chem. Soc. Rev.*, 1996, **25**, 1; N. Ya. Turova, E. P. Turevskaya, V. G. Kessler and M. I. Yanovskaya, *J. Sol-Gel Sci. Technol.*, 1994, **2**, 17.
3 A. I. Yanovskii, N. Ya. Turova, N. I. Koslova and Yu. T. Struchkov, *Koord. Khim.*, 1987, **13**, 242.
4 R. A. Sinclair, W. B. Gleason, R. A. Newmark, J. R. Hill, P. Lyon and J. D. Stevens, in *Chemical Processing of Advanced Materials*, eds. L. L. Hence and J. K. West, Wiley, New York, 1992, p. 207.
5 D. C. Bradley, H. Chudzynska, D. M. Frigo, M. E. Hammond, M. B. Hursthouse and M. A. Mazid, *J. Chem. Soc., Chem. Commun*, 1988, 1258; D. C. Bradley, H. Chudzynska, D. M. Frigo, M. E. Hammond, M. B. Hursthouse and M. A. Mazid, *Polyhedron*, 1990, **9**, 719.
6 O. Poncelet, W. J. Sartain, L. G. Hubert-Pfalzgraf, K. Folting and K. G. Caulton, *Inorg. Chem.*, 1989, **28**, 263.
7 R. W. Wu, Ph.D. Thesis, Queen Mary and Westfield College, University of London, 1991.
8 S. A. Sangokoya, W. T. Pennington, J. Byers-Hill, G. H. Robinson and R. D. Rogers, *Organometallics*, 1993, **12**, 2429.
9 A preliminary report was presented at the Pacifichem-95 International Conference, Honolulu, Hawaii, December, 1995.
10 M. Cesari, *Gazz. Chim. Ital.*, 1980, **110**, 365.
11 N. Ya. Turova, A. I. Yanovskii, V. G. Kessler, N. I. Kozlova and Yu. T. Struchkov, *Zh. Neorg. Khim.*, 1991, **36**, 2497.
12 D. C. Bradley, R. C. Mehrotra, D. P. Gaur, *Metal Alkoxides*, Academic Press, New York, 1978, p. 80.
13 D. C. Bradley, *Coord. Chem. Rev.*, 1967, **2**, 299; see also ref. 15, pp. 150–167.
14 H. Holloway, Ph.D. Thesis, Birkbeck College, University of London, 1959.
15 J. A. Darr, S. R. Drake, M. B. Hursthouse and K. M. A. Malik, *Inorg. Chem.*, 1993, **32**, 5704.
16 N. Walker and D. Stuart, *Acta Crystallogr., Sect A*, 1983, **39**, 158.
17 A. C. T. North, D. C. Phillips and F. S. Matthews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
18 Programs for Crystal Structure Analysis (Release 97–2), G. M. Sheldrick, Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, 1998; G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467; G. M. Sheldrick, SHELXL-93, University of Göttingen, 1993.
19 L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565.