

close donor atoms, and *p* orbitals (that are perpendicular to each other and the *sp*-hybrid axis) to bind N(9<sup>l</sup>) and O(1<sup>ll</sup>) weakly.

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## Structures of Three Aluminum Alkoxide Complexes having the Formula [Al(OR)<sub>2</sub>(acac)]<sub>n</sub>

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**Abstract.** Compound (I): 1,1-bis(acetylacetonato)-bis( $\mu$ -trimethylsiloxy)-2,2-bis(trimethylsiloxy)-dialuminum(III), [Al<sub>2</sub>(C<sub>3</sub>H<sub>7</sub>O)<sub>2</sub>(C<sub>3</sub>H<sub>9</sub>OSi)<sub>4</sub>], *M<sub>r</sub>* = 608.95, trigonal, *P*3<sub>1</sub>21, *a* = 11.170 (9), *c* = 25.87 (3) Å, *V* = 2795 Å<sup>3</sup>, *Z* = 3, *D<sub>x</sub>* = 1.09 g cm<sup>-3</sup>, Mo *K*α, λ = 0.71069 Å, μ = 2.4 cm<sup>-1</sup>, *F*(000) = 983.86, room temperature, *R* = 0.0622 for 1320 unique observed reflections. Compound (II): acetylacetonatobis(triphenylsiloxy)aluminum(III), [Al(C<sub>3</sub>H<sub>7</sub>O)<sub>2</sub>(C<sub>18</sub>H<sub>15</sub>OSi)<sub>2</sub>], *M<sub>r</sub>* = 676.9, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 16.05 (1), *b* = 8.961 (5), *c* = 26.42 (2) Å, β = 104.78 (5)°, *V* = 3674.4 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.22 g cm<sup>-3</sup>, Mo *K*α, λ = 0.71069 Å, μ = 1.6 cm<sup>-1</sup>, *F*(000) = 1423.81, room temperature, *R* = 0.0597 for 2934 unique observed reflections. Compound (III): 1,1,2-tris(acetylacetonato)-1,2;1,2;2,3;2,3-tetra- $\mu$ -isopropoxy-3,3-diisopropoxytrialuminum(III), [Al<sub>3</sub>(C<sub>3</sub>H<sub>7</sub>O)<sub>6</sub>(C<sub>5</sub>H<sub>7</sub>O)<sub>3</sub>], *M<sub>r</sub>* = 731.9, monoclinic, *P*2<sub>1</sub>, *a* = 9.77 (2), *b* = 24.81 (2), *c* = 9.98 (1) Å, β = 115.7 (1)°, *V* = 2179 Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.11 g cm<sup>-3</sup>,

Mo *K*α, λ = 0.71069 Å, μ = 1.33 cm<sup>-1</sup>, *F*(000) = 791.89, room temperature, *R* = 0.0740 for 2335 unique observed reflections. (I) is a symmetric molecule containing tetrahedral and octahedral Al sites on a twofold axis. (II) is a distorted tetrahedral monomer. (III) is a linear trimer containing one tetrahedral and two octahedral Al sites. The complexes studied contain varying degrees of steric crowding about the Al atom, and this steric crowding results in distortions of the geometry at each of the Al sites.

**Introduction.** In previous years, considerable research has been devoted towards understanding the structures of aluminum alkoxide complexes (Bradley, Mehrotra & Gaur, 1978). A unifying theme of this work is the tendency of Al to maximize its coordination number, resulting in associated molecules containing tetrahedral and octahedral metal centers. Although five-coordinate complexes have been postulated (Mehrotra & Mehrotra, 1961), structural evidence to support their

Table 1. *Experimental details*

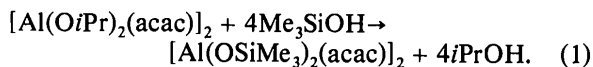
	(I)	(II)	(III)
Crystal habit	Prismatic	Prismatic	Prismatic
size (mm)	0.3 × 0.3 × 0.3	0.3 × 0.3 × 0.3	0.2 × 0.2 × 0.4
Lattice parameters			
No. reflections	12	12	16
2θ range (°)	4.7–11.3	5.2–18.2	5.1–18.8
Reflection range			
h	–8 to 13	0 to 15	0 to 11
k	–13 to 13	0 to 10	0 to 27
l	–28 to 28	–29 to 29	–11 to 11
Max. sinθ/λ (Å <sup>-1</sup> )	0.538	0.538	0.538
Check reflections	003 112	312 004	111 161
variation (%)	3 1	3 1	1 1
Reflections			
collected	13 416	5286	3137
unique observed	1320	2934	2335
Observed criterion	I > 3σ(I)	I > 2σ(I)	I > 1.25σ(I)
No. parameters	164	433	417
R	0.0622	0.0597	0.0740
R <sub>w</sub>	0.0696	0.0564	0.0887
Weighting factor (g)	0.001	0.0005	0.0027
w <sup>-1</sup> = σ <sup>2</sup> (F) + gF <sup>2</sup>			
Fourier difference peaks			
min. (e Å <sup>-3</sup> )	–0.456	–0.310	–0.400
max. (e Å <sup>-3</sup> )	0.360	0.260	0.420
Max. Δ/σ	0.000	0.739	0.013

existence is rare (Bonamico & Dessy, 1968; Thewalt & Stollmaier, 1982).

In an effort to understand the way in which steric crowding of the ligands about Al affects the geometry of the Al site, three aluminum alkoxide complexes were prepared and their structures investigated.

#### Compound (I)

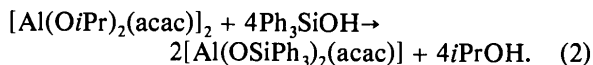
(I) is synthesized by reacting four equivalents of trimethylsilanol with bis(acetylacetonato)tetraisopropoxydialuminum (Wengrovius, Going & Garbaskas, 1984):



<sup>1</sup>H NMR, <sup>29</sup>Si NMR, and field desorption mass spectrometry of (I) support a dimeric structure with both terminal and bridging siloxy groups present. A symmetric dimeric product containing one acetylacetonate and one trimethylsiloxy ligand per Al as well as bridging trimethylsiloxy ligands between the two Al sites is consistent with this evidence. This model involves five-coordinate Al which, owing to the rarity of this coordination, would pose some interesting geometrical considerations.

#### Compound (II)

(II) is synthesized by reacting four equivalents of triphenylsilanol with bis(acetylacetonato)tetraisopropoxydialuminum (Wengrovius *et al.*, 1984):

Table 2. *Atom coordinates (×10<sup>4</sup>) and temperature factors (Å<sup>2</sup> ×10<sup>3</sup>) for (I)*

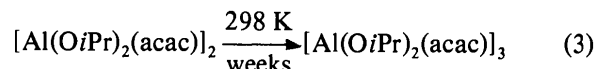
$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U <sub>eq</sub>
Al(1)	5149 (4)	5149 (5)	0	51 (2)
Al(2)	2633 (4)	2633 (4)	0	51 (2)
Si(1)	7842 (3)	5250 (3)	543 (1)	69 (2)
Si(2)	3330 (3)	4836 (3)	968 (1)	60 (2)
O(1)	6578 (7)	5338 (7)	308 (2)	71 (4)
O(2)	3649 (5)	4323 (5)	403 (2)	45 (3)
O(3)	3460 (6)	1764 (7)	360 (2)	58 (4)
O(4)	1110 (7)	1849 (7)	446 (2)	65 (4)
C(1)	9418 (11)	6374 (11)	184 (4)	100 (7)
C(2)	7466 (11)	3446 (11)	515 (5)	144 (10)
C(3)	8083 (12)	5788 (12)	1215 (4)	120 (9)
C(4)	4736 (12)	6678 (10)	1072 (4)	106 (8)
C(5)	3405 (10)	3738 (10)	1486 (3)	84 (6)
C(6)	1634 (13)	4727 (13)	952 (4)	134 (11)
C(7)	2855 (12)	685 (11)	620 (4)	63 (7)
C(8)	3660 (11)	26 (11)	779 (4)	92 (8)
C(9)	1487 (12)	114 (11)	817 (3)	81 (7)
C(10)	699 (12)	766 (15)	719 (4)	75 (8)
C(11)	–750 (11)	149 (12)	927 (4)	129 (9)

<sup>1</sup>H NMR, <sup>29</sup>Si NMR and field desorption mass spectrometry of (II) support a tetrahedral monomeric structure. It is of interest to determine the differences which result in a dimeric complex for (I) and a monomeric complex for (II).

#### Compound (III)

(III) is synthesized by allowing bis(acetylacetonato)tetraisopropoxydialuminum to age for several weeks at 298 K (Wengrovius *et al.*, 1984) as shown in equation (3). During this process, the liquid dimer becomes a crystalline trimer.



<sup>1</sup>H NMR and field desorption mass spectrometry of (III) support a trimeric molecular structure. Several structures, both linear and cyclic, are consistent with this evidence.

**Experimental.** All data collected at room temperature using a Nicolet P3F automated single-crystal diffractometer and Mo Kα radiation. Compounds (I) and (III) were sealed in glass capillaries under an inert atmosphere owing to their sensitivity to moisture. Compound (II) is air and moisture stable. *D<sub>m</sub>* values not determined. Each of the structures solved by direct methods using the *SHELXTL* program package (Sheldrick, 1981). All H positions located by a difference Fourier synthesis and, in final stages of refinement (on *F*), constrained to have bond lengths of 0.96 Å, appropriate bond angles, and isotropic thermal parameters of 0.06 Å<sup>2</sup>. All non-hydrogen atoms treated as anisotropic except where noted for (III). No absorption correction necessary for any of the structures. No correction for secondary extinction. Details of the data collection are in Table 1.

**Discussion.** Atomic coordinates and bond lengths and angles are in Tables 2–7.\* Thermal-ellipsoid plots (50% probability) showing the numbering schemes are in Figs. 1–3.

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39442 (46 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Bond lengths (Å) and angles (°) for (I)

Al(1)–O(2)	1.788 (6)	Al(1)–O(1)	1.700 (8)
Al(1)–O(2a)	1.788 (6)	Al(1)–O(1a)	1.700 (8)
Al(2)–O(3)	1.886 (8)	Al(2)–O(2)	1.948 (6)
Al(2)–O(2a)	1.948 (6)	Al(2)–O(4)	1.872 (7)
Al(2)–O(4a)	1.872 (7)	Al(2)–O(3a)	1.886 (8)
Si(1)–C(1)	1.823 (10)	Si(1)–O(1)	1.584 (9)
Si(1)–C(3)	1.817 (10)	Si(1)–C(2)	1.843 (13)
Si(2)–C(4)	1.882 (9)	Si(2)–O(2)	1.672 (6)
Si(2)–C(6)	1.836 (16)	Si(2)–C(5)	1.846 (11)
O(4)–C(10)	1.271 (15)	O(3)–C(7)	1.244 (12)
C(7)–C(9)	1.423 (17)	C(7)–C(8)	1.478 (21)
C(10)–C(11)	1.506 (17)	C(9)–C(10)	1.418 (24)
O(1)–Al(1)–O(2)	111.7 (3)	O(2)–Al(2)–O(2a)	78.3 (3)
O(1)–Al(1)–O(1a)	115.8 (5)	O(2)–Al(1)–O(1a)	113.7 (4)
O(2)–Al(1)–O(2a)	86.8 (4)	O(1)–Al(1)–O(2a)	113.7 (4)
O(2)–Al(2)–O(3)	92.1 (3)	O(1a)–Al(1)–O(2a)	111.7 (3)
O(2)–Al(2)–O(4)	94.4 (2)	O(3)–Al(2)–O(4)	91.1 (3)
O(3)–Al(2)–O(2a)	89.0 (3)	O(4)–Al(2)–O(2a)	172.6 (3)
O(3)–Al(2)–O(3a)	178.6 (4)	O(4)–Al(2)–O(3a)	87.9 (3)
O(2a)–Al(2)–O(3a)	92.1 (3)	O(2)–Al(2)–O(3a)	89.0 (3)
O(2)–Al(2)–O(4a)	172.6 (3)	O(3)–Al(2)–O(4a)	87.9 (3)
O(4)–Al(2)–O(4a)	93.0 (4)	O(2a)–Al(2)–O(4a)	94.4 (2)
O(3a)–Al(2)–O(4a)	91.1 (3)	O(1)–Si(1)–C(1)	110.3 (5)
O(1)–Si(1)–C(2)	109.3 (5)	C(1)–Si(1)–C(2)	110.3 (6)
O(1)–Si(1)–C(3)	109.6 (6)	C(1)–Si(1)–C(3)	109.1 (4)
C(2)–Si(1)–C(3)	108.3 (6)	O(1)–Si(2)–C(4)	107.2 (4)
O(2)–Si(2)–C(5)	108.6 (5)	C(4)–Si(2)–C(5)	109.4 (5)
O(2)–Si(2)–C(6)	110.3 (4)	C(4)–Si(2)–C(6)	110.2 (6)
C(5)–Si(2)–C(6)	111.1 (5)	Al(1)–O(1)–Si(1)	169.2 (6)
Al(1)–O(2)–Al(2)	97.4 (3)	Al(1)–O(2)–Si(2)	129.6 (3)
Al(2)–O(2)–Si(2)	132.8 (3)	Al(2)–O(3)–C(7)	126.6 (8)
Al(2)–O(4)–C(10)	126.8 (10)	O(3)–C(7)–C(8)	117.5 (11)
O(3)–C(7)–C(9)	124.8 (14)	C(8)–C(7)–C(9)	117.4 (10)
C(7)–C(9)–C(10)	120.5 (10)	O(4)–C(10)–C(9)	124.5 (11)
O(4)–C(10)–C(11)	115.3 (14)	C(9)–C(10)–C(11)	120.1 (11)
Al(1)–O(2a)–Al(2)	97.4 (3)		

Table 4. Atom coordinates ( $\times 10^4$ ) and temperature factors ( $\text{Å}^2 \times 10^3$ ) for (II)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}$
Al	2178 (1)	6389 (2)	2441 (1)	38 (1)
Si(1)	3059 (1)	4783 (2)	3557 (1)	38 (1)
Si(2)	1975 (1)	5071 (2)	1310 (1)	39 (1)
O(1)	1109 (2)	7122 (4)	2355 (1)	46 (1)
O(2)	2715 (2)	8123 (4)	2394 (1)	53 (1)
O(3)	2229 (2)	5225 (4)	1941 (1)	47 (1)
O(4)	2533 (2)	5665 (4)	3044 (1)	52 (1)
C(1)	893 (3)	8490 (6)	2269 (2)	48 (2)
C(2)	–46 (4)	8809 (8)	2175 (3)	79 (3)
C(3)	1479 (4)	9616 (6)	2248 (2)	59 (2)
C(4)	2344 (4)	9400 (6)	2302 (2)	55 (2)
C(5)	2909 (5)	10684 (7)	2238 (3)	90 (3)
C(6)	3456 (3)	6180 (6)	4095 (2)	43 (2)
C(7)	3348 (4)	7692 (7)	4016 (3)	73 (3)
C(8)	3639 (5)	8717 (7)	4424 (3)	94 (4)
C(9)	4038 (4)	8230 (8)	4913 (3)	72 (3)
C(10)	4162 (4)	6739 (7)	5000 (2)	60 (3)
C(11)	3873 (3)	5713 (6)	4600 (2)	46 (2)
C(12)	2346 (3)	3404 (6)	3776 (2)	42 (2)
C(13)	1940 (3)	3735 (7)	4168 (2)	55 (2)
C(14)	1378 (4)	2712 (8)	4309 (2)	66 (3)
C(15)	1216 (4)	1384 (7)	4067 (3)	73 (3)
C(16)	1610 (4)	1016 (7)	3683 (3)	76 (3)
C(17)	2166 (4)	2011 (6)	3541 (2)	60 (2)
C(18)	3981 (3)	3745 (6)	3403 (2)	43 (2)
C(19)	4343 (4)	2470 (7)	3676 (2)	56 (2)
C(20)	5022 (4)	1705 (8)	3559 (3)	77 (3)
C(21)	5357 (4)	2224 (10)	3166 (3)	88 (4)
C(22)	5018 (4)	3468 (10)	2888 (3)	83 (3)
C(23)	4336 (3)	4207 (7)	2999 (2)	64 (3)
C(24)	1818 (3)	6977 (3)	1008 (2)	41 (2)
C(25)	2452 (4)	7683 (6)	822 (2)	67 (3)
C(26)	2361 (5)	9163 (7)	655 (3)	86 (3)
C(27)	1641 (5)	9946 (7)	662 (3)	84 (3)
C(28)	999 (5)	9263 (7)	835 (3)	75 (3)
C(29)	1086 (4)	7783 (6)	1002 (2)	56 (2)
C(30)	937 (3)	4016 (5)	1101 (2)	39 (2)
C(31)	546 (4)	3433 (6)	1475 (2)	56 (2)
C(32)	–235 (4)	2664 (7)	1329 (3)	74 (3)
C(33)	–634 (4)	2468 (7)	807 (3)	83 (3)
C(34)	–259 (4)	3019 (7)	434 (3)	71 (3)
C(35)	515 (3)	3779 (6)	583 (2)	54 (2)
C(36)	2845 (3)	4052 (5)	1101 (2)	42 (2)
C(37)	3534 (3)	3425 (6)	1470 (2)	53 (2)
C(38)	4169 (4)	2628 (7)	1319 (3)	74 (3)
C(39)	4137 (4)	2443 (7)	799 (3)	76 (3)
C(40)	3470 (4)	3063 (6)	425 (3)	68 (3)
C(41)	2837 (4)	3859 (6)	572 (2)	56 (2)

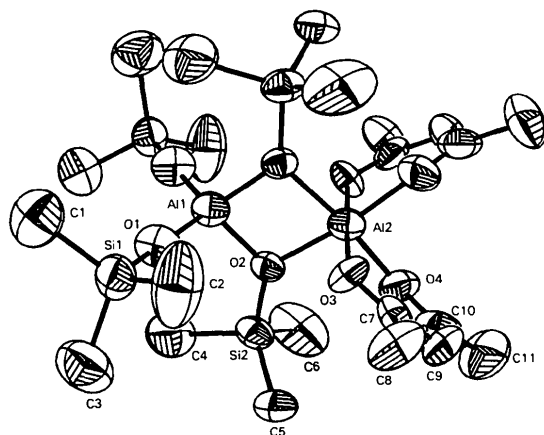


Fig. 1. Thermal-ellipsoid (50% probability) plot of (I).

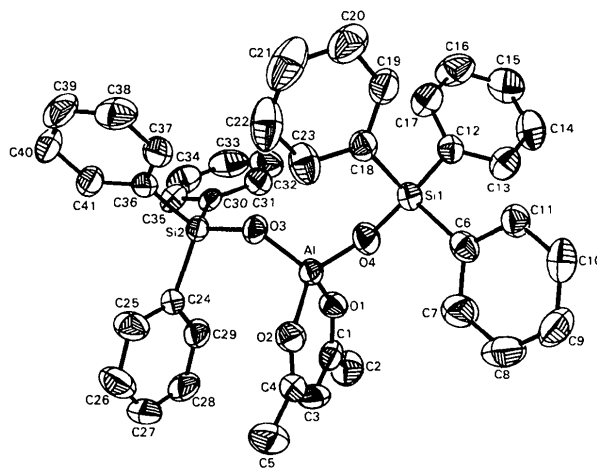


Fig. 2. Thermal-ellipsoid (50% probability) plot of (II).

Table 5. Bond lengths (Å) and angles (°) for (II) (except phenyl groups)

Al—O(1)	1.797 (4)	Al—O(2)	1.796 (4)
Al—O(3)	1.700 (4)	Al—O(4)	1.680 (4)
Si(1)—O(4)	1.610 (3)	Si(1)—C(6)	1.879 (5)
Si(1)—C(12)	1.872 (5)	Si(1)—C(18)	1.879 (6)
Si(2)—O(3)	1.619 (3)	Si(2)—C(24)	1.874 (5)
Si(2)—C(30)	1.872 (5)	Si(2)—C(36)	1.866 (6)
O(1)—C(1)	1.279 (7)	O(2)—C(4)	1.284 (6)
C(1)—C(2)	1.491 (8)	C(1)—C(3)	1.390 (8)
C(3)—C(4)	1.373 (8)	C(4)—C(5)	1.501 (9)
O(1)—Al—O(2)	97.7 (2)	O(1)—Al—O(3)	111.1 (2)
O(2)—Al—O(3)	111.1 (2)	O(1)—Al—O(4)	110.0 (2)
O(2)—Al—O(4)	110.2 (2)	O(3)—Al—O(4)	115.3 (2)
O(4)—Si(1)—C(6)	108.3 (2)	O(4)—Si(1)—C(12)	110.8 (2)
C(6)—Si(1)—C(12)	108.8 (2)	O(4)—Si(1)—C(18)	109.4 (2)
C(6)—Si(1)—C(18)	111.1 (2)	C(12)—Si(1)—C(18)	108.5 (2)
O(3)—Si(2)—C(24)	109.4 (2)	O(3)—Si(2)—C(30)	108.5 (2)
C(24)—Si(2)—C(30)	108.8 (2)	O(3)—Si(2)—C(36)	109.6 (2)
C(24)—Si(2)—C(36)	110.5 (2)	C(30)—Si(2)—C(36)	110.1 (2)
Al—O(1)—C(1)	125.5 (3)	Al—O(2)—C(4)	125.2 (4)
Al—O(3)—Si(2)	143.3 (2)	Al—O(4)—Si(1)	165.2 (3)
O(1)—C(1)—C(2)	115.5 (5)	O(1)—C(1)—C(3)	123.1 (5)
C(2)—C(1)—C(3)	121.3 (5)	C(1)—C(3)—C(4)	124.8 (5)
O(2)—C(4)—C(3)	123.6 (5)	O(2)—C(4)—C(5)	116.1 (5)
C(3)—C(4)—C(5)	120.3 (5)	Si(1)—C(6)—C(7)	122.5 (4)
Si(1)—C(6)—C(11)	120.7 (4)	Si(1)—C(12)—C(13)	121.9 (4)
Si(1)—C(12)—C(17)	121.9 (4)	Si(1)—C(18)—C(19)	122.7 (4)
Si(1)—C(18)—C(23)	121.2 (4)	Si(2)—C(24)—C(25)	122.3 (4)
Si(2)—C(24)—C(29)	120.3 (4)	Si(2)—C(30)—C(31)	120.4 (3)
Si(2)—C(30)—C(35)	123.0 (4)	Si(2)—C(36)—C(37)	120.8 (4)
Si(2)—C(36)—C(41)	122.4 (4)		

**Compound (I)**

The results indicate that the symmetric dimeric structure postulated from NMR and mass-spectrometric evidence is incorrect. The actual structure is a symmetric molecule containing tetrahedral and octahedral Al sites on a twofold axis. The large thermal parameters associated with the C atoms of the methyl groups are evidence of the motion associated with these groups.

**Compound (II)**

The structure is a distorted tetrahedral monomer. The bond lengths and angles for the phenyl groups are not unusual.

**Compound (III)**

The structure of this complex is a linear trimer containing one tetrahedral and two octahedral Al sites. The isopropoxy group described by O(7), C(18), C(19), and C(20) is disordered. Because of this, these three C atoms have been refined isotropically and the C(18)—C(19) and C(19)—C(20) bond lengths fixed at 1.50 Å.

Compounds (I), (II), and (III) show a preference for tetrahedral and octahedral coordination around Al, and avoid geometries with a coordination number of five. Although all three compounds have the same empirical formula,  $[\text{Al}(\text{OR})_2(\text{acac})]_n$ , the molecular formula depends on the size of the alkoxy or siloxy ligand. Thus, when this ligand is a large triphenylsiloxy, the molecule is a monomer, (II). With ligands containing progressively smaller cone angles, trimethylsiloxy and isopropoxy, the molecules are a dimer, (I), and a trimer, (III), respectively.

Table 6. Atom coordinates ( $\times 10^4$ ) and temperature factors ( $\text{Å}^2 \times 10^3$ ) for (III)

$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j a_i^* a_j^* a_i a_j$			
	x	y	z
Al(1)	4514 (3)	5886	7264 (3)
Al(2)	3701 (3)	4783 (1)	6110 (3)
Al(3)	3051 (3)	6860 (1)	5726 (3)
O(1)	4175 (6)	5461 (2)	5599 (6)
O(2)	3870 (6)	5226 (3)	7738 (6)
O(3)	2588 (6)	6259 (2)	6387 (6)
O(4)	4914 (6)	6568 (3)	6467 (6)
O(5)	6604 (7)	5706 (2)	8135 (7)
O(6)	4840 (7)	6234 (3)	9074 (6)
O(7)	2880 (10)	7448 (3)	6439 (11)
O(8)	2227 (7)	6898 (3)	3821 (7)
O(9)	1560 (7)	4900 (3)	5149 (7)
O(10)	3552 (8)	4405 (3)	4408 (8)
O(11)	3225 (8)	4129 (3)	6821 (8)
O(12)	5795 (7)	4568 (3)	7030 (8)
C(1)	5789 (12)	5313 (5)	4298 (13)
C(2)	4448 (11)	5622 (4)	4308 (10)
C(3)	2999 (12)	5571 (4)	2890 (10)
C(4)	2205 (11)	4830 (5)	8776 (14)
C(5)	3779 (12)	5080 (4)	9087 (11)
C(6)	5088 (14)	4715 (5)	10090 (13)
C(7)	-141 (12)	6256 (6)	4987 (14)
C(8)	1155 (10)	6093 (4)	6402 (11)
C(9)	1010 (14)	6323 (6)	7724 (13)
C(10)	7143 (15)	7093 (6)	7965 (15)
C(11)	6306 (11)	6784 (5)	6547 (12)
C(12)	6005 (13)	7134 (5)	5233 (13)
C(13)	7616 (11)	5724 (4)	9459 (10)
C(14)	9054 (11)	5454 (5)	9799 (13)
C(15)	7350 (12)	5975 (5)	10538 (12)
C(16)	5982 (11)	6240 (4)	10292 (10)
C(17)	5879 (13)	6565 (5)	11499 (12)
C(18)	1534 (27)	7939 (11)	7457 (31)
C(19)	2856 (25)	7642 (10)	7422 (28)
C(20)	3746 (34)	8138 (11)	8151 (34)
C(21)	101 (17)	7471 (7)	2481 (19)
C(22)	1657 (15)	7297 (6)	2779 (14)
C(23)	1853 (20)	7154 (8)	1415 (14)
C(24)	543 (14)	4639 (5)	4053 (13)
C(25)	-1047 (12)	4741 (6)	3769 (16)
C(26)	889 (14)	4291 (5)	3170 (13)
C(27)	2373 (14)	4167 (5)	3376 (12)
C(28)	2744 (20)	3803 (6)	2431 (18)
C(29)	3868 (15)	3700 (5)	7092 (15)
C(30)	3083 (18)	3230 (5)	7312 (19)
C(31)	5436 (17)	3634 (5)	7319 (17)
C(32)	6318 (14)	4092 (4)	7245 (16)
C(33)	7949 (16)	4000 (6)	7686 (22)

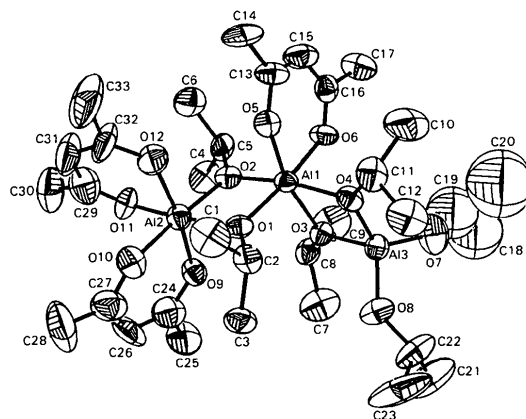
†  $U_{\text{iso}}$ .

Fig. 3. Thermal-ellipsoid (50% probability) plot of (III).

Table 7. Bond lengths (Å) and angles (°) for (III)

Al(1)—O(1)	1.872 (7)	Al(1)—O(2)	1.887 (7)
Al(1)—O(3)	1.933 (6)	Al(1)—O(4)	1.980 (7)
Al(1)—O(5)	1.894 (7)	Al(1)—O(6)	1.900 (7)
Al(2)—O(1)	1.873 (7)	Al(2)—O(2)	1.907 (7)
Al(2)—O(9)	1.907 (6)	Al(2)—O(10)	1.890 (8)
Al(2)—O(11)	1.907 (8)	Al(2)—O(12)	1.919 (7)
Al(3)—O(3)	1.766 (7)	Al(3)—O(4)	1.794 (6)
Al(3)—O(7)	1.662 (10)	Al(3)—O(8)	1.716 (7)
C(32)—C(33)	1.476 (20)	O(1)—C(2)	1.479 (13)
O(2)—C(5)	1.434 (14)	O(3)—C(8)	1.466 (13)
O(4)—C(11)	1.430 (13)	O(5)—C(13)	1.262 (9)
O(6)—C(16)	1.243 (9)	O(7)—C(19)	1.103 (31)
O(8)—C(22)	1.498 (15)	O(9)—C(24)	1.289 (12)
O(10)—C(27)	1.306 (12)	O(11)—C(29)	1.206 (14)
O(12)—C(32)	1.268 (13)	C(1)—C(2)	1.522 (17)
C(2)—C(3)	1.513 (11)	C(4)—C(5)	1.559 (16)
C(5)—C(6)	1.532 (14)	C(7)—C(8)	1.487 (14)
C(8)—C(9)	1.499 (19)	C(10)—C(11)	1.502 (17)
C(11)—C(12)	1.492 (18)	C(13)—C(14)	1.456 (15)
C(13)—C(15)	1.363 (18)	C(15)—C(16)	1.412 (16)
C(16)—C(17)	1.489 (17)	C(18)—C(19)	1.500 (40)
C(19)—C(20)	1.500 (36)	C(21)—C(22)	1.481 (23)
C(22)—C(23)	1.496 (24)	C(24)—C(25)	1.474 (18)
C(24)—C(26)	1.377 (20)	C(26)—C(27)	1.407 (20)
C(27)—C(28)	1.461 (24)	C(29)—C(30)	1.464 (22)
C(29)—C(31)	1.456 (23)	C(31)—C(32)	1.447 (20)
O(3)—Al(1)—O(4)	74.4 (3)	O(1)—Al(1)—O(2)	77.5 (3)
O(1)—Al(1)—O(3)	96.0 (3)	O(2)—Al(1)—O(3)	99.5 (3)
O(1)—Al(1)—O(4)	96.6 (3)	O(2)—Al(1)—O(4)	171.2 (2)
O(4)—Al(1)—O(5)	91.4 (3)	O(1)—Al(1)—O(5)	90.9 (3)
O(2)—Al(1)—O(5)	95.2 (3)	O(3)—Al(1)—O(5)	164.9 (3)
Al(3)—Al(1)—O(6)	88.0 (2)	O(1)—Al(1)—O(6)	172.7 (3)
O(2)—Al(1)—O(6)	95.3 (3)	O(3)—Al(1)—O(6)	86.7 (3)
O(4)—Al(1)—O(6)	90.7 (3)	O(5)—Al(1)—O(6)	88.1 (3)
O(1)—Al(2)—O(2)	77.0 (3)	O(1)—Al(2)—O(10)	97.7 (3)
O(1)—Al(2)—O(9)	94.2 (3)	O(2)—Al(2)—O(9)	90.7 (3)
O(2)—Al(2)—O(10)	174.6 (4)	O(9)—Al(2)—O(10)	89.0 (3)
O(10)—Al(2)—O(11)	88.6 (4)	O(1)—Al(2)—O(11)	173.7 (4)
O(2)—Al(2)—O(11)	96.8 (3)	O(9)—Al(2)—O(11)	85.7 (3)
O(1)—Al(2)—O(12)	92.4 (3)	O(2)—Al(2)—O(12)	94.1 (3)
O(9)—Al(2)—O(12)	172.6 (3)	O(10)—Al(2)—O(12)	86.7 (3)
O(11)—Al(2)—O(12)	88.1 (3)	O(3)—Al(3)—O(4)	83.3 (3)
O(4)—Al(3)—O(7)	116.7 (4)	O(3)—Al(3)—O(7)	119.4 (5)
O(3)—Al(3)—O(8)	112.7 (3)	O(4)—Al(3)—O(8)	112.6 (4)
Al(1)—O(1)—Al(2)	103.5 (3)	Al(1)—O(1)—C(2)	126.3 (5)
Al(2)—O(1)—C(2)	129.7 (6)	Al(1)—O(2)—Al(2)	101.6 (4)
Al(1)—O(2)—C(5)	128.1 (5)	Al(2)—O(2)—C(5)	129.6 (6)
Al(1)—O(3)—Al(3)	102.5 (3)	Al(1)—O(3)—C(8)	127.3 (5)
Al(3)—O(3)—C(8)	130.0 (5)	Al(1)—O(4)—Al(3)	99.7 (3)
Al(1)—O(4)—C(11)	130.2 (5)	Al(3)—O(4)—C(11)	130.0 (6)
Al(1)—O(5)—C(13)	132.2 (8)	Al(1)—O(6)—C(16)	130.1 (7)
Al(3)—O(7)—C(19)	144.1 (16)	Al(3)—O(8)—C(22)	136.3 (8)
Al(2)—O(9)—C(24)	128.7 (8)	Al(2)—O(10)—C(27)	129.1 (9)
Al(2)—O(11)—C(29)	130.4 (10)	Al(2)—O(12)—C(32)	127.4 (7)
O(1)—C(2)—C(1)	110.5 (8)	O(1)—C(2)—C(3)	110.1 (9)
C(1)—C(2)—C(3)	114.2 (9)	O(2)—C(5)—C(4)	111.7 (7)
O(2)—C(5)—C(6)	112.8 (10)	C(4)—C(5)—C(6)	111.5 (9)
O(3)—C(8)—C(7)	109.7 (10)	O(3)—C(8)—C(9)	110.9 (8)
C(7)—C(8)—C(9)	111.4 (10)	O(4)—C(11)—C(10)	111.1 (11)
O(4)—C(11)—C(12)	110.4 (8)	C(10)—C(11)—C(12)	110.6 (10)
O(5)—C(13)—C(14)	117.8 (10)	O(5)—C(13)—C(15)	120.8 (9)
C(14)—C(13)—C(15)	121.4 (8)	C(13)—C(15)—C(16)	124.4 (8)
O(6)—C(16)—C(15)	123.0 (10)	O(6)—C(16)—C(17)	116.8 (9)
O(7)—C(19)—C(18)	125.9 (19)	O(7)—C(19)—C(20)	124.0 (29)
C(18)—C(19)—C(20)	84.8 (22)	O(8)—C(22)—C(21)	114.0 (14)
O(8)—C(22)—C(23)	110.4 (13)	C(21)—C(22)—C(23)	114.3 (12)
O(9)—C(24)—C(25)	116.0 (12)	O(9)—C(24)—C(26)	123.0 (12)
C(25)—C(24)—C(26)	121.0 (10)	C(24)—C(26)—C(27)	124.4 (10)
O(10)—C(27)—C(26)	121.2 (12)	O(10)—C(27)—C(28)	114.1 (12)
C(26)—C(27)—C(28)	124.6 (11)	O(11)—C(29)—C(30)	118.8 (14)
O(11)—C(29)—C(31)	123.0 (12)	C(30)—C(29)—C(31)	118.1 (12)
C(29)—C(31)—C(32)	120.9 (11)	O(12)—C(32)—C(31)	122.3 (13)
O(12)—C(32)—C(33)	119.9 (11)	C(31)—C(32)—C(33)	117.0 (11)

The Al—O bond lengths in each molecule are very dependent on steric crowding imposed by neighboring ligands. Accordingly, the Al—O bond lengths in the alkoxy and siloxy groups of (I), (II), and (III) fall into three general categories: (1) 1.872–1.980 Å found in the bridging isopropoxy and trimethylsiloxy groups bound to the octahedral Al sites in (I) and (II); (2) 1.766–1.794 Å found in the same bridging alkoxy and siloxy groups bound to the tetrahedral Al sites in (I) and (III); and (3) 1.662–1.716 Å found in the terminal alkoxy and siloxy groups which occupy tetrahedral positions in (I), (II), and (III). The shorter Al—O bond lengths in the bridging, tetrahedrally coordinated trimethylsiloxy ligands in (I) are nearly identical to similarly coordinated trimethylsiloxy groups (Al—O = 1.79 Å) in tetrabromobis(trimethylsiloxy)-dialuminum (Bonamico & Dessy, 1967). The average Al—O bond lengths (mean value 1.897 Å) and angles (mean value 89.2°) associated with the acetylacetonate ligands in octahedral sites of (I) and (III) are very similar to those found in octahedral tris(acetylacetonato)aluminum (1.892 Å and 91.8°) (Hon & Pfluger, 1973). The O(1)—Al—O(2) bond angle found within the tetrahedral acetylacetonate ligand in (II) is larger (97.7°), and the Al—O bond lengths are shorter (1.797 Å), than their octahedral counterparts. All Al—O bond lengths for the octahedral Al sites in (I) and (III) are approximately equal. In all three molecules, distortions in the tetrahedral and octahedral geometries are imposed by steric repulsions between the ligands.

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