

Short Communication

The Molecular Structure of a Dinuclear Mixed-Bridge Organoaluminium Compound, $(\text{CH}_3)_4\text{Al}_2(\mu\text{-CH}_3)(\mu\text{-OC}(\text{CH}_3)_3)$, by Gas-Phase Electron Diffraction

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One mole of acetone reacts stoichiometrically with one mole of trimethyl aluminium dimer in hydrocarbon solvents at ambient temperature to yield a hemialkoxide, $(\text{CH}_3)_3\text{Al}_2\text{OC}(\text{CH}_3)_3$ (I).¹ ¹H-NMR and IR spectra show that the two aluminium atoms are bridged by the *tert*-butoxide group and one of the methyl groups as indicated in Fig. 1. Since only one mixed-bridge organoaluminium compound, *viz.* $(\text{CH}_3)_4\text{Al}_2(\mu\text{-CH}_3)(\mu\text{-NPh}_2)$ Ph = phenyl, appears to have been studied by diffraction methods,² we decided to determine the molecule structure of I by gas-phase electron diffraction for comparison with the structures of the related compounds $(\text{CH}_3)_4\text{Al}_2(\mu\text{-CH}_3)_2$ ³ and $(\text{CH}_3)_4\text{Al}_2(\mu\text{-OC}(\text{CH}_3)_3)_2$.⁴

A sample of I was synthesized as described by Jeffery and Mole.¹ The gas-phase electron diffraction data were recorded on a Balzers Eldigraph KDG-2 instrument⁵ with a metal inlet system at ambient temperature. Exposures were made with nozzle-to-plate distances of about 50 and 25 cm. Structure refinements were based on six photographic plates from each set. Optical densities were recorded on the Snoopy densitometer and processed by standard procedures.⁶ Atomic scattering factors were taken from Ref. 7. Backgrounds were drawn as least-squares adjusted polynomials to the difference between total experimental and calculated molecular intensity curves. The final modified molecular intensity curves are shown in Fig. 2.

Structure refinements were based on a molecular model of C_s symmetry as indicated in Fig. 1. In order to reduce the number of structure parameters it was assumed that the molecular frame consisting of the two Al atoms O, C1

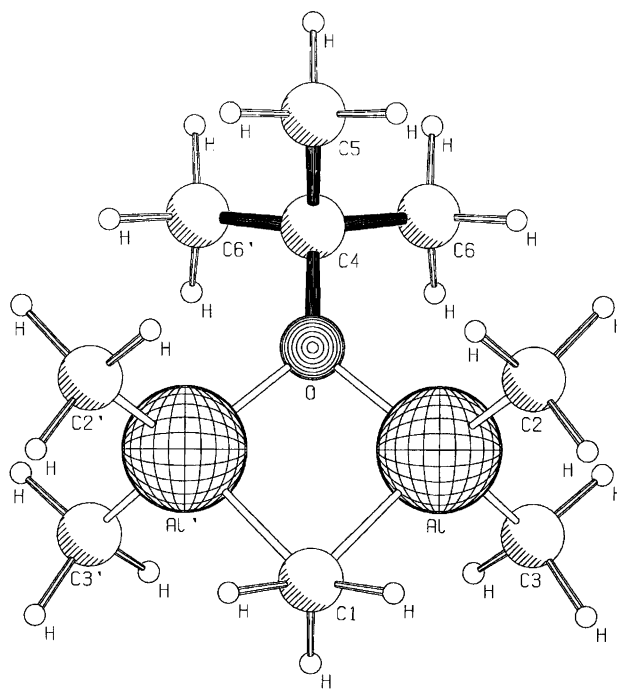


Fig. 1. Molecular model of $(\text{CH}_3)_4\text{Al}_2(\mu\text{-CH}_3)(\mu\text{-OC}(\text{CH}_3)_3)$, point group C_s , drawn with the computer program PLUTON.⁸

and C4 and the four terminal methyl groups has C_{2v} symmetry. Methyl groups were assumed to have C_{3v} symmetry with the symmetry axes coinciding with the neighbouring C–C, *viz.* C–Al bonds, and fixed in staggered orientations as indicated in Fig. 1. Similarly the *tert*-butyl group was assumed to have C_{3v} symmetry with the symmetry axis coinciding with the C4–O bond.

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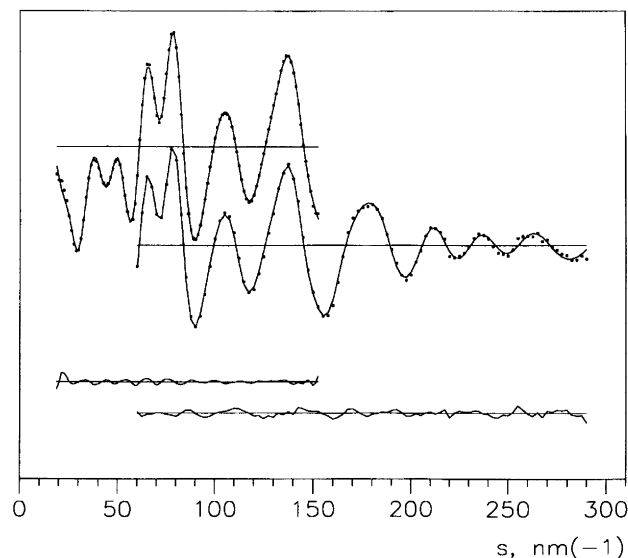


Fig. 2. Experimental (dots) and calculated (lines) modified molecular intensity curves for $(\text{CH}_3)_4\text{Al}_2(\mu\text{-CH}_3)(\mu\text{-OC}(\text{CH}_3)_3)$.

After these assumptions have been made, the structure is determined by 11 independent structure parameters, for instance the bond distances Al–O, Al–Cl, Al–C2, O–C4, C4–C5 and a mean C–H bond distance, and the valence angles $\angle \text{Al–O–Al}$, $\angle \text{C2–Al–C3}$, $\angle \text{O–Al–C2}$, $\angle \text{O–C4–C5}$, $\angle \text{C4–C5–H}$ and $\angle \text{Al–C2–H}$. Start values for root mean-square vibrational amplitudes were taken from earlier GED studies of $(\text{CH}_3)_4\text{Al}_2(\mu\text{-CH}_3)_2$ ³ and $(\text{CH}_3)_4\text{Al}_2(\mu\text{-OC}(\text{CH}_3)_3)_2$.⁴ The vibrational amplitudes of five bond distances, as well as the Al...Al distance, were refined as independent parameters. Distances between nonbonded atoms were divided into seven sets, and the amplitudes in each set were refined with constant differences. Both angles $\angle \text{C4–C5–H}$ and $\angle \text{Al–C2–H}$ refined to values close to 113° with estimated standard deviations of about 4° . In the final cycles $\angle \text{C4–C5–H}$ was fixed at 113° . The refinements converged to the best values listed in Table 1. Since the refinements were carried out with a diagonal weight matrix, the estimated standard deviations calculated by the program have been multiplied by a factor of three to include the added uncertainty due to data correlation⁹ and expanded to include a scale uncertainty of 0.1%. Experimental and calculated radial distribution curves are compared in Fig. 3.

In Table 2 we compare some bond distances and valence angles in I with the corresponding parameters in $(\text{CH}_3)_4\text{Al}_2(\mu\text{-CH}_3)_2$ ³ and $(\text{CH}_3)_4\text{Al}_2(\mu\text{-OC}(\text{CH}_3)_3)_2$.⁴ Interestingly the bond distance from Al to the bridging methyl group appears to be shorter in the mixed-bridge compound than in the trimethyl aluminium dimer.

The $\angle \text{Al–C}_b\text{–Al}$ valence angle in the electron-deficient compound $(\text{CH}_3)_4\text{Al}_2(\mu\text{-CH}_3)_2$ is $75.5(1)^\circ$ and the Al...Al distance is 261.9(5) pm, as compared to the Al–Al bond distance of 266.0(1) pm in $\text{R}_2\text{Al–AlR}_2$, $\text{R} = \text{CH}(\text{Si}(\text{CH}_3)_3)_2$.¹⁰ The geometry thus suggests that

Table 1. Structure parameters of $(\text{CH}_3)_4\text{Al}_2(\mu\text{-CH}_3)(\mu\text{-OC}(\text{CH}_3)_3)$. Bond distances (r_a) and root mean-square vibrational amplitudes (l) in pm, valence angles in $^\circ$.^a

	Bond distances	R.m.s. vibrational amplitudes
Al–O	184.2(12)	5.7(14)
Al–Cl	210.3(10)	7.1(18)
Al–C2	194.8(7)	5.5(15)
O–C4	147(4)	[4.0]
C4–C5	152.3(12)	4.9(20)
C–H	110.6(2)	8.0(4)
Nonbonded distances		
Al–Al'	271.8(12)	8.8(10)
Al–C2'	408.5(15)	20.9(13) ^d
Al–C4	303(4)	16.5(23) ^e
Al–C6	333.2(24)	20.6(13)
Al–C5	380.2(18)	14.8(13) ^f
Al–C6'	421.9(13)	11.8(13) ^f
O–C2	319.0(10)	16.5(23) ^e
O–C6	246.2(21)	7.8(5)
C1–C2	326.6(23)	18.9(23) ^e
C2–C4	403(3)	18.9(13) ^d
C2–C6	425.8(24)	19.8(13) ^f

Valence angles

$\angle \text{Al–O–Al}$	95.1(10)
$\angle \text{O–Al–Cl}$	92.2(7)
$\angle \text{Al–Cl–Al}$	80.5(6)
$\angle \text{C2–Al–C3}$	117.4(14)
$\angle \text{O–Al–C2}$	114.6(7)
$\angle \text{C1–Al–C2}$	107.4(10)
$\angle \text{Al–C2–H}$	113.3(18)
$\angle \text{O–C4–C5}$	110.9(24)
$\angle \text{C4–C5–H}$	[113.0]

R-factors^c 0.040 (50 cm) 0.081 (25 cm) 0.049 (total)

^a Estimated standard deviations in parentheses in units of the last digit. Parameters in square brackets have been adjusted, but not refined. See text. ^b Mean value.

^c $R = [\sum W(I_{\text{obs}} - I_{\text{calc}})^2 / \sum W(I_{\text{obs}})^2]^{1/2}$.

^{d–f} Denotes sets of amplitudes which were refined with equal shifts.

Table 2. Interatomic distances and valence angles in $(\text{CH}_3)_4\text{Al}_2(\mu\text{-X})(\mu\text{-Y})$, X, Y = CH₃ or OC(CH₃)₃.^a

	X=Y=CH ₃ ^b	X=CH ₃ Y=OC(CH ₃) ₃ ^c	X=Y= OC(CH ₃) ₃ ^d
Al–C _b	214.0(4)	210.3(10)	–
Al–O	–	184.2(12)	186.4(6)
Al–C _t	195.7(3)	194.8(7)	196.2(15)
Al–Al	261.9(5)	271.8(12)	282(2)
$\angle \text{Al–C}_b$	75.5(1)	80.5(6)	–
$\angle \text{Al–O–Al}$	–	95.1(10)	98.1(7)
$\angle \text{X–Al–Y}$	104.5(1)	92.2(7)	81.9(7)
$\angle \text{C}_t\text{–Al–C}_t$	117.3(15)	117.4(14)	121.7(17)

^a b = bridge, t = terminal. ^b Ref. 3. ^c This work. ^d Ref. 4.

there is direct bonding between the Al atoms. In the electron-precise compound $(\text{CH}_3)_4\text{Al}_2(\mu\text{-OC}(\text{CH}_3)_3)_2$ the valence angle at the bridging O atom is $98.1(7)^\circ$, the

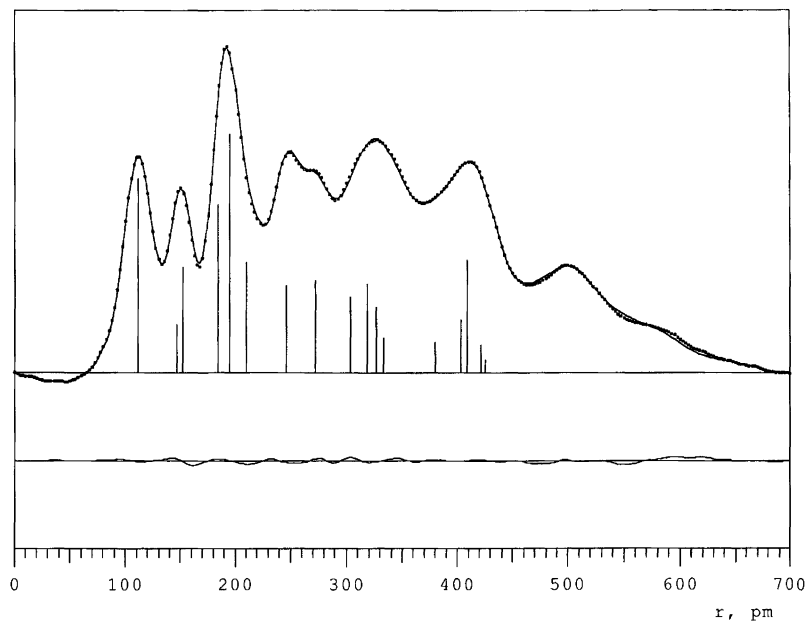


Fig. 3. Experimental (dots) and calculated (lines) radial distribution curves for $(\text{CH}_3)_4\text{Al}_2(\mu\text{-CH}_3)(\mu\text{-OC}(\text{CH}_3)_3)$. Artificial damping constant $k=25 \text{ pm}^2$. Below: Difference curve.

valence angle $\angle \text{O-Al-O}$ is $81.9(7)^\circ$ and the $\text{Al}\cdots\text{Al}$ distance is $282(2) \text{ pm}$, indicating that the interaction between the Al atoms is repulsive as expected. In the mixed-bridge compound the $\text{Al}\cdots\text{Al}$ distance at $271.6(15) \text{ pm}$ is exactly the average of the distances in $(\text{CH}_3)_4\text{Al}_2(\mu\text{-CH}_3)_2^3$ and $(\text{CH}_3)_4\text{Al}_2(\mu\text{-OC}(\text{CH}_3)_3)_2^4$. The valence angle at the bridging C atom is significantly larger than in the analogue with two methyl bridges, while the valence angle at the O atom is probably smaller than in the analogue with two bridging *tert*-butoxide groups.

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