

# The Molecular Structure of Dimethylaluminium Chloride Dimer, $[(CH_3)_2AlCl]_2$ , Redetermined by Gas Phase Electron Diffraction

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$[(CH_3)_2AlCl]_2$  has been studied by gas phase electron diffraction. The scattering pattern is consistent with a molecular model of  $D_{2h}$  symmetry with bridging Cl atoms. The main molecular parameters are Al–C = 1.935(4) Å, Al–Cl = 2.303(3) Å,  $\angle C-Al-C = 126.9(0.8)^\circ$  and  $\angle Cl-Al-Cl = 89.4(0.5)^\circ$ . The Al–C bond is significantly *shorter* than the Al–C (terminal) bond in  $[(CH_3)_3Al]_2$ , the Al–Cl bond significantly *longer* than the Al–Cl (bridge) bond in  $[AlCl_3]_2$ .

As part of our study of associated organoaluminium compounds we have carried out a reinvestigation of dimeric  $(CH_3)_2AlCl$  which was first investigated by means of gas phase electron diffraction more than 30 years ago.<sup>1</sup>

## EXPERIMENTAL AND CALCULATION PROCEDURE<sup>2,3</sup>

$[(CH_3)_2AlCl]_2$  was prepared from  $[(CH_3)_3Al]_2$  and  $[AlCl_3]_2$  and was distilled twice before use. The electron scattering pattern was recorded on Balzers Eldiograph KD-G2. The sample reservoir was maintained at about 25°C, corresponding to a vapor pressure of about 15 mmHg.<sup>4</sup> Exposures were made with nozzle to photographic plate distances of 50 cm and 25 cm. The optical densities of four plates from the first set were recorded at  $\Delta s = 0.125 \text{ \AA}^{-1}$  intervals, the optical densities of five plates from the last set were recorded at  $\Delta s = 0.250 \text{ \AA}^{-1}$  intervals. The optical densities were converted into intensities and the data processed in the usual way.<sup>2</sup>

Every other modified molecular intensity point obtained from the 50 cm plates is shown in Fig. 1A, the modified molecular intensity points obtained from the 25 cm plates are shown in Fig. 2A.

Theoretical intensity curves were calculated from:

$$I^{AlC}(s) = \sum_{i \neq j} \frac{|f_i(s)| |f_j(s)|}{|f_{Al}(s)| |f_C(s)|} \cos [\eta_i(s) - \eta_j(s)]$$

$$\frac{\sin (R_{ij}s)}{R_{ij}} \exp (-\frac{1}{2} l_{ij}^2 s^2)$$

The sum extends over all atom pairs  $i, j$  in the molecule.  $R_{ij}$  is the internuclear distance,  $l_{ij}$  the root mean square amplitude of vibration.  $f_j(s) = |f_j(s)| \exp [i\eta_j(s)]$  is the complex atomic scattering factor of atom  $j$ .

The molecular structure was refined by least-squares calculations on the intensity data with a non-diagonal weight matrix and a separately refined scale factor for the intensity data obtained for each nozzle-to-plate distance.<sup>3</sup> The

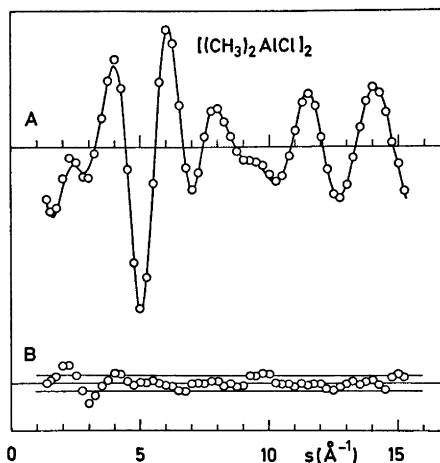


Fig. 1. A, O: Experimental modified molecular intensity points from  $s = 1.50$  to  $15.26 \text{ \AA}^{-1}$ . Only every other experimental point is shown. Full line: Theoretical intensity curve calculated for best model. B: Difference points. Note: The scale of B is twice that of A.

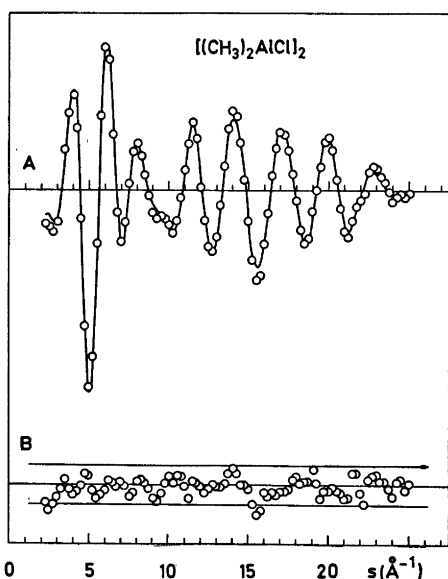


Fig. 2. A, O: Experimental modified molecular intensity points from  $s = 2.25$  to  $25.00 \text{ \AA}^{-1}$ . Full line: Theoretical intensity curve calculated for best model. B: Difference points. Note: The scale of B is twice that of A.

standard deviations obtained were expanded to take into account an estimated uncertainty of 0.1 % in the electron wavelength.

Radial distribution functions were calculated by Fourier inversion of experimental and theoretical intensity curves after multiplication with the artificial damping function  $\exp(-ks^2)$ . The experimental intensity functions were then spliced to each other and to the theoretical curve calculated for the best model below  $s = 1.50 \text{ \AA}^{-1}$ .

## STRUCTURE ANALYSIS

A molecular model of  $[(\text{CH}_3)_2\text{AlCl}]_2$  is shown in Fig. 3. It was assumed that:

- (i) The molecular symmetry is  $D_{2h}$ ;

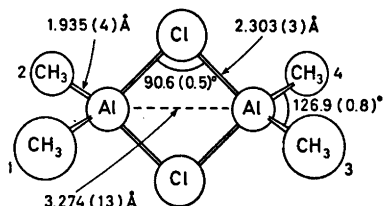


Fig. 3. Molecular model of  $[(\text{CH}_3)_2\text{AlCl}]_2$ .

(ii) The methyl groups have  $C_{3v}$  symmetry with the threefold axes coinciding with the Al-C bonds;

(iii) The angle of rotation of the methyl groups about the Al-C bonds is such that the H atoms are staggered with respect to the bonds radiating from the Al atom.

The molecular structure is then determined by six independent parameters, e.g. the three bond distances Al-Cl, Al-C, and C-H and the three valence angles  $\angle \text{Cl-Al-Cl}$ ,  $\angle \text{C-Al-C}$ , and  $\angle \text{Al-C-H}$ . Vibrational effects ("shrinkage") were neglected.

Least squares refinement of the six structure parameters and eleven vibrational amplitudes converged to the values listed in Table 1.

The vibrational amplitude of the  $\text{C}_1\cdots\text{C}_2$

Table 1. Bond distances, valence angles, and root mean square vibrational amplitudes ( $l$ ) of  $[(\text{CH}_3)_2\text{AlCl}]_2$ . (Estimated standard deviations in parentheses). For numbering of the atoms consult Fig. 3. The distances are given as  $r_a$ . The angles have not been corrected for shrinkage.

	$R(\text{\AA})$	$l(\text{\AA})$
Bond distances		
C-H	1.104(8)	0.081(9)
Al-C	1.935(4)	0.054(4)
Al-Cl	2.303(3)	0.069(2)
Nonbonded distances		
Al...Al	3.274(13)	0.106(38)
Al...C	4.487(13)	0.182(16)
Al...H	2.528(14)	0.095(11)
Cl...Cl	3.241(13)	0.077(11)
Cl...C	3.447(5)	0.124(5)
Cl...H	3.467(17)	0.74(11) <sup>a</sup>
Cl...H	3.697(14)	0.74(11) <sup>a</sup>
Cl...H	4.417(9)	0.45(11)
$\text{C}_1\cdots\text{C}_2$	3.462(15)	0.133 <sup>b</sup>
$\text{C}_1\cdots\text{C}_3$	5.004(24)	0.43(14)
$\text{C}_1\cdots\text{C}_4$	6.085(14)	0.160(33)
Valence angles (deg.)		
$\angle \text{Al-C-H}$	109.5(1.1)	
$\angle \text{C-Al-C}$	126.9(0.8)	
$\angle \text{Cl-Al-Cl}$	89.4(0.5)	
$\angle \text{Al-Cl-Al}$	90.6(0.5)	

<sup>a</sup> These amplitudes were assumed equal. <sup>b</sup> Assumed value, see text.

distance was fixed at the value found in monomeric  $(\text{CH}_3)_3\text{Al}$ ,<sup>5</sup>  $l(\text{C}_1\cdots\text{C}_2)=0.133(5)$  Å, because refinement did not converge when it was allowed to vary.

Modified molecular intensity curves calculated for the best model are shown in Fig. 1A and Fig. 2A. The difference between experimental and calculated intensities is shown in Fig. 1B and Fig. 2B. The agreement is satisfactory except in the region below  $s=5$  Å<sup>-1</sup>. It is possible that the disagreement in this region is due to the neglect of shrinkage. The data in this range were given a very low weight during the least squares refinement.

An experimental radial distribution function is shown in Fig. 4A, the difference between this curve and a theoretical curve calculated for the best model is shown in Fig. 4B.

## DISCUSSION

The molecular structure of  $[(\text{CH}_3)_2\text{AlCl}]_2$  may be compared with the molecular structure of the related molecules  $[(\text{CH}_3)_3\text{Al}]_2$ ,<sup>5</sup>  $[(\text{CH}_3)\text{AlCl}_2]_2$ ,<sup>6</sup> and  $[\text{AlCl}_3]_2$ .<sup>7</sup>

The Al—C bond in  $[(\text{CH}_3)_2\text{AlCl}]_2$  is significantly *shorter* than the terminal Al—C bonds in  $[(\text{CH}_3)_3\text{Al}]_2$  or monomeric  $(\text{CH}_3)_3\text{Al}$ , in either compound Al—C<sub>t</sub>=1.957(3) Å. Similarly the  $\angle\text{C—Al—C}$  angle in  $[(\text{CH}_3)_2\text{AlCl}]_2$  is significantly larger than in  $[(\text{CH}_3)_3\text{Al}]_2$ . Both differences indicate that the atomic orbitals on Al used for bonding to C<sub>t</sub> have more *s*-character in  $[(\text{CH}_3)_2\text{AlCl}]_2$  than in  $[(\text{CH}_3)_3\text{Al}]_2$ .

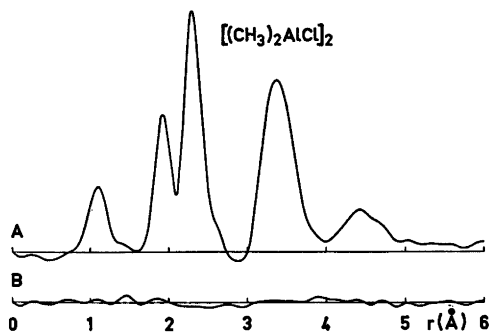


Fig. 4. A: Experimental radial distribution curve. Artificial damping constant  $k=0.0025$  Å<sup>2</sup>. B: Difference between the experimental curve and a theoretical curve calculated for the best model.

The Al—Cl bond in  $[(\text{CH}_3)_2\text{AlCl}]_2$  is significantly longer than the bridging Al—Cl bond in  $[\text{AlCl}_3]_2$ , 2.252(4) Å, or in  $[(\text{CH}_3)\text{AlCl}_2]_2$  where the two crystallographically nonequivalent Al—Cl<sub>b</sub> bonds are 2.25(1) and 2.26(1) Å, respectively. The reason is probably that exchange of the terminal  $\text{CH}_3$  groups in  $[(\text{CH}_3)_2\text{AlCl}]_2$  with more electronegative Cl atoms increases the acceptor strength of the Al atom. Since there is no detectable difference between the Al—Cl<sub>b</sub> distances in  $[(\text{CH}_3)\text{AlCl}_2]_2$  and  $[\text{AlCl}_3]_2$ , it would appear that the effect of the introduction of a second terminal Cl atom on each Al atom is considerably less than the effect of the first.

Despite the difference in bond distances the angles in the central  $\text{Al}_2\text{Cl}_2$  rings are very similar in the three compounds; all angles are very close to 90°.

The large amplitudes obtained for the Cl...H distances in  $[(\text{CH}_3)_2\text{AlCl}]_2$  suggest that the barrier to internal rotation of the methyl groups is of the order of or less than the thermal energy available.

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