Molecular Structure of Dimethylaluminium Fluoride Tetramer by Electron Diffraction

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Summary The molecular structure of $[Me_2AlF]_4$ has been determined by gas phase electron diffraction.

Diethylaluminium fluoride is tetrameric in freezing and in boiling benzene,[1] and dimethylaluminium fluoride is tetrameric in freezing benzene.[2] Spectroscopic studies have shown that both compounds contain eight-membered rings of alternating aluminium and bridging fluorine atoms.[1,2] Their degree of association in the gas phase is unknown.

We have recorded the electron scattering pattern from gaseous dimethylaluminium fluoride from $s = 1{\cdot}50$ to $s = 30{\cdot}00$ Å^{-1} with source and nozzle at 65 °C. The data show that the tetramer concentration in the gas must have been at least 95% and confirm the cyclic structure. The bond distances and valence angles obtained at the present stage of least-squares refinement on the intensity data are listed in the Table (e.s.d.s. in parentheses).

C–H	1·116(13) Å
Al–C	1·942(6) Å
Al–F	1·808(4) Å
∠C–Al–C	127(3)°
∠F–Al–F	94(2)°
∠Al–F–Al	148(2)°

Since the sum of the F–Al–F and Al–F–Al valence angles is less than 270°, the eight-membered ring cannot be planar. We have found that models of C_{4v} or D_{2d} symmetry (of the latter there are two, one with the F atoms, the other with the Al atoms in the mirror planes) are incompatible with the electron diffraction data. The three upper curves in the Figure show experimental radial distribution curves (full line) along with theoretical radial distribution curves (dashed line) calculated for the best models of C_{4v} and D_{2d} symmetry. All three models show serious disagreement between experimental and theoretical curves in the region above 3·5 Å. Satisfactory agreement between experimental and theoretical curves is obtained with a "chair-boat"[3] model of C_s symmetry with two Al atoms in the mirror plane. The lower curves in the Figure show an experimental radial distribution (RD) curve obtained by Fourier inversion of the experimental intensity curve after it has been spliced to the theoretical intensity curve calculated for the best model below $s = 1{\cdot}5$ Å^{-1} and the difference between this experimental RD curve and a theoretical RD curve calculated for the best model of C_s symmetry. The squares-error sum obtained by least-squares refinement on this model was less than 50% of that obtained by refinement of the other models mentioned above. We believe, however, that equally good agreement could have been obtained for other models of low symmetry. In any case it is clear that the molecule is far from rigid.

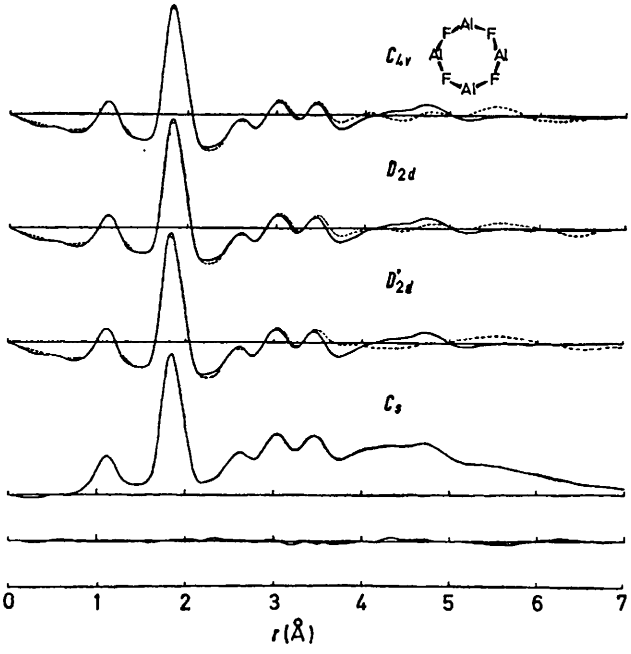

Figure.

The Al–F–Al angle in $[Me_2AlF]_4$ is very much smaller than the corresponding angle in $K[Et_3AlFAlEt_3]$, 180°,[4] but appears similar to the valence angle at the bridging F atoms in polymeric Me_3SnF.[5] The Al–F bond distances in $[Me_2AlF]_4$ and $K[Et_3AlFAlEt_3]$ are very similar. In the latter compound Al–F is 1·820(3) Å.

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