The Molecular Structure of Dimethylaminodichloroalane

Dimer Determined by Gas Phase Electron Diffraction

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The molecular structure of $[Cl_2AlN(CH_3)_2]_2$ has been determined by gas phase electron diffraction. The scattering pattern is consistent with a model of D_{2h} symmetry with bridging $N(CH_3)_2$ groups. The main molecular parameters are $Al-Cl = 2.106(4)$ Å, $Al-N = 1.961(6)$ Å, $N-C = 1.479(4)$ Å, $\angle Cl-Al-Cl = 118.2(1.5)°$, $\angle Al-N-Al = 92.5(0.4)°$.

Cl_2AlNMe_2 (Me = CH$_3$) is dimeric in boiling benzene [1] (by molecular weight) and in the gas phase [2] (by mass spectroscopy). Infrared absorption spectra show that association occurs through the NMe_2 group rather than through the Cl atoms.[2] As part of our study of associated aluminium compounds we have determined the molecular structure of the dimer for comparison with the molecular structures of the $AlCl_3$ dimer and dimeric Me_2AlNMe_2. The structure of the first of these compounds has been determined by gas phase electron diffraction by Hedberg and coworkers,[3] the structure of the second has been determined by X-ray crystallography by Hess and coworkers [4] and by Smith and coworkers.[5]

The $Al-N$ bond distance in the addition complex Cl_3AlNMe_3[6,7] is about 0.14 Å shorter than in the complex Me_3AlNMe_3 [8] and the bridging $Al-Cl$ bond in dimeric $AlCl_3$ is about 0.05 Å shorter than in $[Me_2AlCl]_2$.[9] Both shortenings are reasonably ascribed to the inductive effect of the terminal Cl atoms. It was therefore anticipated that the bridging $Al-N$ bond in $[Cl_2AlNMe_2]_2$ would be found to be several hundredths of an Å unit shorter than in $[Me_2AlNMe_2]_2$.

Since the Me_2N group generally forms stronger bridges than the Cl atom, it was further

anticipated that the terminal $Al-Cl$ bond in $[Cl_2AlNMe_2]_2$ would be found to be longer than in $[AlCl_3]_2$.

EXPERIMENTAL AND CALCULATION PROCEDURE

The sample of $[Cl_2AlNMe_2]_2$, which had been prepared from $[Me_2AlNMe_2]_2$ and $AlCl_3$ in hexane,[10] was a gift from Dr. Heinz Hoberg. The electron scattering pattern was recorded on the Oslo electron diffraction unit [11] with a nozzle temperature of about 175 °C. Exposures were made with nozzle to photographic plate distances of about 48 and 26 cm. The optical densities of six plates from the first set were recorded at $\Delta s = 0.125$ Å^{-1} intervals, the optical densities of five plates from the second set were recorded at $\Delta s = 0.250$ Å^{-1} intervals and the
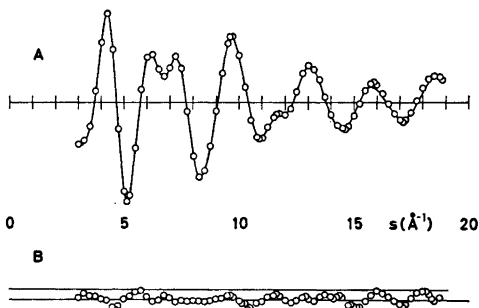

Fig. 1. A, O: Experimental modified molecular intensity points from $s = 3.00$ to 18.75 Å^{-1}. Only every other experimental point is shown. Full line: Theoretical intensity curve calculated for the best model. B, O: Difference points. The full lines indicate the estimated uncertainty (three standard deviations) of the experimental points. Note: The scale of B is twice that of A.
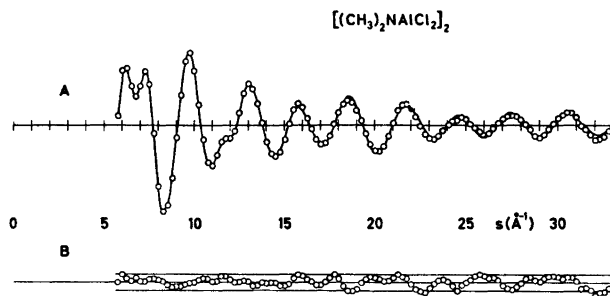
$$[(CH_3)_2NAlCl_2]_2$$

Fig. 2. A, O: Experimental modified molecular intensity points from $s = 5.75$ to 33.00 Å^{-1}. Full line: Theoretical intensity curve calculated for the best model. B, O: Difference points. The full lines indicate the estimated uncertainty (three standard deviations) of the experimental points. *Note:* The scale of B is twice that of A.

data processed as described by Andersen *et al.*[12]

Every other modified molecular intensity point obtained from the 48 cm plates is shown in Fig. 1A, while the modified molecular intensity points obtained from the 26 cm plates are shown in Fig. 2A.

Theoretical intensity curves were calculated from

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

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

The sum extends over all atom pairs 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.

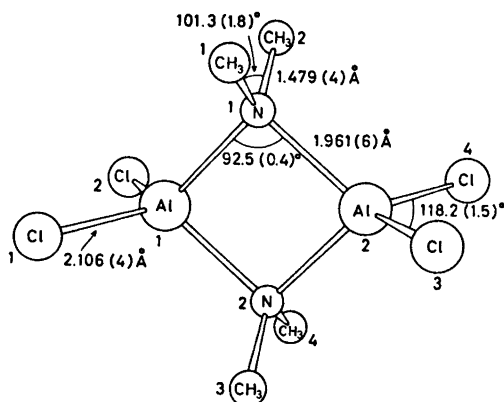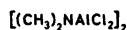The molecular structure was refined by least-squares calculations on the intensity data with a non-diagonal weight matrix and a separately refined scale factor for the two sets of intensity data.[13] The standard deviations obtained were expanded to take into account an estimated uncertainty of 0.1 % in the electron wavelength.

Radial distribution functions were calculated by Fourier inversion of experimental and theoretical modified molecular intensity curves after multiplication with the artificial damping function exp $(-ks^2)$. The experimental intensity curves were then first spliced to each other and to the theoretical curve calculated for the best model below $s = 3.00$ Å^{-1}.

STRUCTURE ANALYSIS

A molecular model of $[Cl_2AlNMe_2]_2$ is shown in Fig. 3. It was assumed that:

(i)   The molecular symmetry is D_{2h}.
(ii) The Me groups have C_{3v} symmetry with the C_3 axes coinciding with the N – C bonds.
(iii) The angle of rotation of the Me groups about the C – N bonds is such that the H atoms are staggered with respect to the bonds radiating from the N atom.

The molecular structure is then determined by eight independent parameters, *e.g.* the four bond distances Al – Cl, Al – N, N – C, and C – H and the four valence angles $\angle$ Cl – Al – Cl, $\angle$ Al – N – Al, $\angle$ C – N – C, and $\angle$ N – C – H. In addition the shrinkages of the two longest intramolecular distances $Cl_1 \cdots Cl_3$ and $Cl_1 \cdots Cl_4$ were refined as independent parameters. All other shrinkages were neglected.

Simultaneous least squares refinement of these ten parameters and fourteen vibrational
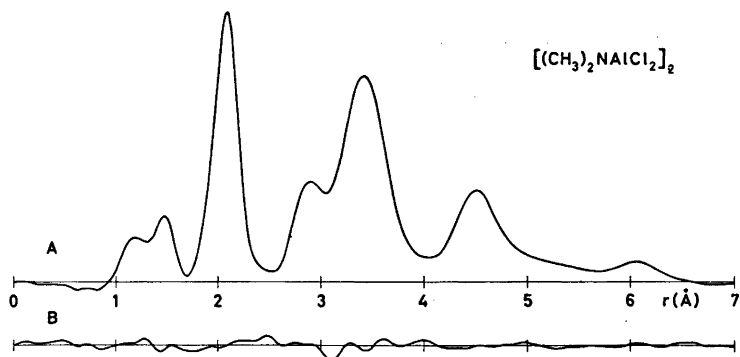

Fig. 3. Molecular model of $[Cl_2AlN(CH_3)_2]_2$.

$[(CH_3)_2NAlCl_2]_2$

Fig. 4. A: Experimental radial distribution curve. Artificial damping constant $k = 0.0025$ Å². B: Difference between the experimental curve and a theoretical curve calculated for the best model.

Table 1. Internuclear distances, valence angles and root mean square vibrational amplitudes (l) of $[Cl_2AlNMe_2]_2$. (Estimated standard deviations in parentheses.) For numbering of the atoms consult Fig. 3. The distances are listed as r_a. The angles have not been corrected for shrinkage.

	R (Å)	l (Å)
Bond distances		
Al – Cl	2.106(4)	0.058(2)
Al – N	1.961(6)	0.088(7)
N – C	1.479(4)	0.058(4)
C – H	1.160(8)	0.075(8)
Nonbonded distances		
$Cl_1 \cdots Cl_2$	3.614(30)	0.192(34)
$Cl_1 \cdots Cl_3$	5.231(44)	0.427(43)
$Cl_1 \cdots Cl_4$	6.082(13)	0.197(10)
$Cl_1 \cdots Al_1$	4.312(14)	0.392(71)
$Cl_1 \cdots N_1$	3.368(8)	0.141(7)[a]
$Cl_1 \cdots C_1$	3.456(13)	0.141(7)[a]
$Cl_1 \cdots C_2$	4.496(7)	0.159(7)
$Al_1 \cdots Al_2$	2.833(13)	0.073(10)[b]
$Al_1 \cdots C_1$	2.929(8)	0.158(11)
$N_1 \cdots N_2$	2.713(16)	0.073(10)[b]
$N_1 \cdots C_3$	3.825(15)	0.232(64)
$C_1 \cdots C_2$	2.288(30)	0.083(17)
$C_1 \cdots C_3$	4.588(33)	0.350[c]
$C_1 \cdots C_4$	5.127(19)	0.300[c]
Shrinkages (Å)		
$Cl_1 \cdots Cl_3$	− 0.234(51)	
$Cl_1 \cdots Cl_4$	0.085(22)	
Valence angles (deg)		
$\angle Cl – Al – Cl$	118.2(1.5)	
$\angle Al – N – Al$	92.5(0.4)	
$\angle C – N – C$	101.3(1.8)	
$\angle N – C – H$	104.1(3.4)	

[a] $l(Cl_1 \cdots N_1)$ and $l(Cl_1 \cdots C_1)$ were assumed equal.
[b] $l(Al_1 \cdots Al_2)$ and $l(N_1 \cdots N_2)$ were assumed equal.
[c] These amplitudes were not refined.

amplitudes converged to the values listed in Table 1. Attempts to refine the amplitudes of the distances $Cl_1 \cdots C_1$, $N_1 \cdots N_2$, $C_1 \cdots C_3$, and $C_1 \cdots C_4$ lead to divergence. These amplitudes were therefore constrained as indicated in the table. Since $l(C_1 \cdots C_3)$ and $l(C_1 \cdots C_4)$ were correlated with some of the parameters that were refined (in particular the correlation coefficient between $<C – N – C$ and $l(C_1 \cdots C_3)$ is 0.42) the standard deviations listed in the table are those obtained in a final least-squares cycle in which $l(C_1 \cdots C_3)$ and $l(C_1 \cdots C_4)$ were allowed to vary.

Modified molecular intensity curves calculated for the best model are shown in Figs. 1A and 2A. The difference between experimental and calculated intensities is shown in Figs. 1B and 2B. The agreement is satisfactory.

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

DISCUSSION

Contrary to expectation the Al – N bond distance in $[Cl_2AlNMe_2]_2$ is found to be exactly equal to the Al – N bond distance found in $[Me_2AlNMe_2]_2$ by X-ray crystallography [4,5] (mean value 1.961). However, taking into consideration the combined uncertainties of the structure determinations as well as the fact that correction for thermal motion in the crystal would increase the bond distance in $[Me_2AlNMe_2]_2$, it is clear that a difference of 0.04 Å or less cannot be ruled out.

The Al−Cl bond distance in [Cl$_2$AlNMe$_2$]$_2$, 2.106(4) Å, is significantly longer than the terminal Al−Cl bonds in [AlCl$_3$]$_2$,[3] 2.065(2) Å, and significantly shorter than in Cl$_3$AlNMe$_3$,[7] 2.121(4) Å.

The other bond distances and valence angles fall in the expected range.

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Received October 4, 1974.