

Methylation analyses. The polysaccharide (2 mg) was methylated by Hakomori's method^{3,7} and recovered by dialysis against running tap-water and concentration to dryness. The product was then treated on the steam-bath with 90 % formic acid (1 ml) for 30 min, diluted with 10 volumes of water, and returned to the steam-bath for 3,5 h. The solution was then concentrated to a small volume and the remaining formic acid was removed by co-distillation with additional water (3×5 ml). Finally the product was either reduced with sodium borodeuteride and acetylated or part of it was treated in this way, and the remainder was acetylated without reduction as described below. For acetylation pyridine (1 ml) and acetic anhydride (1 ml) were added to the dry product and after 10 min at room temperature the flask was moved to the steam-bath for 20 min. The acetylating agents were then removed by co-distillation with toluene (3×5 ml) and the product was examined by GLC.

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The Molecular Structure of Trichlorotrimethylamine-aluminium, $\text{Cl}_3\text{AlN}(\text{CH}_3)_3$ by Gas Phase Electron Diffraction

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Recently we have determined the molecular structures of the complexes $\text{Me}_3\text{AlNMe}_3$ ¹ (Me = CH_3) and H_3AlNMe_3 ² by means of gas phase electron diffraction. We now report the results of a similar study of $\text{Cl}_3\text{AlNMe}_3$. This complex has previously been studied by X-ray crystallography,³ but we hoped to improve on the accuracy.

The electron scattering pattern from gaseous $\text{Cl}_3\text{AlNMe}_3$ was recorded on the Oslo electron diffraction unit⁴ with a nozzle temperature of about 330°C. Exposures were made with a nozzle-to-photographic-plate distance of about 48 cm. The intensity data thus obtained extended from $s=1.50 \text{ \AA}^{-1}$ to $s=18.00 \text{ \AA}^{-1}$. A radial distribution (RD) curve obtained by Fourier inversion of the modified molecular intensity curve⁵ is shown in Fig. 1. A.

The molecular structure was refined under the assumption that the molecular symmetry is C_{3v} with the Cl atoms of the acceptor and the Me groups of the donor staggered with respect to rotation about the Al-N bond (as they are in the crystal). The Me groups were assumed to have C_{3v} symmetry and to be oriented in such a way that the C-H bonds are staggered with respect to the bonds radiating from the N atom. The molecular structure is then determined by seven independent parameters, e.g. the Al-Cl, Al-N, N-C, and C-H bond distances and the $\angle\text{N-Al-Cl}$, $\angle\text{Al-N-C}$, and $\angle\text{N-C-H}$ valence angles. The latter was fixed at 109.8°, the angle found in free NMe_3 .⁶ Since it was anticipated that large amplitude libration about the Al-N bond might lead to an average value of the Cl...C(*trans*) distance that was significantly smaller than that calculated for the equilibrium geometry, the shrinkage of this distance was included in the refinement as an additional independent parameter. The vibrational amplitude of the Al-N bond distance was fixed at the value found

in H_3AlNMe_3 , $l(\text{Al}-\text{N})=0.084$ Å. Vibrational amplitudes between the atoms in the donor were fixed at the values found in free NMe_3 .

Simultaneous least-squares refinement of the six structure parameters, the shrinkage of the $\text{Cl}\cdots\text{C}(\textit{trans})$ distance, and the six most important vibrational amplitudes with a non-diagonal weight matrix⁷ converged to the values listed in Table 1.

Table 1. Bond distances, valence angles and root-mean-square vibrational amplitudes of $\text{Cl}_3\text{AlN}(\text{CH}_3)_3$.

	R (Å)	l (Å)
C-H	1.121(25)	0.081 ^a
N-C	1.516(12)	0.045 ^a
Al-N	1.945(35)	0.084 ^a
Al-Cl	1.121(4)	0.055(10)
$\angle \text{N}-\text{Al}-\text{Cl}$	104.9(0.7)°	
$\angle \text{Al}-\text{N}-\text{C}$	112.6(1.5)°	
$\angle \text{N}-\text{C}-\text{H}$	109.8 ^a	
$\text{Cl}\cdots\text{Cl}$	3.55(2)	0.14(1)
$\text{Cl}\cdots\text{N}$	3.23(2)	0.07(1)
$\text{Cl}\cdots\text{C}(\textit{gauche})$	3.57(3)	0.30(9)
$\text{Cl}\cdots\text{C}(\textit{trans})$	4.51(6)	0.18(5)
$\text{Al}\cdots\text{C}$	2.89(2)	0.11(2)

^a Assumed value, see text.

A theoretical RD-curve calculated for the best model is shown in Fig. 1 A. The good agreement between experimental and theoretical curves shows that the degree of dissociation of the complex in the gas jet must have been negligible.

Shown in Fig. 1 B is a theoretical RD-curve calculated for a model in which the Cl atoms of the acceptor eclipse the Me groups of the donor. This curve shows serious disagreement with the experimental curve in the region of the $\text{Cl}\cdots\text{C}$ distances and may confidently be ruled out.

The value obtained for the Al-N bond distance is in agreement with, but is considerably less accurate than the Al-N bond distance determined by X-ray crystallography, 1.96(1) Å. This bond is significantly shorter than the Al-N bond in H_3AlNMe_3 , 2.06 Å, which in turn is significantly shorter than the Al-N bond in $\text{Me}_3\text{AlNMe}_3$, 2.10 Å. This variation

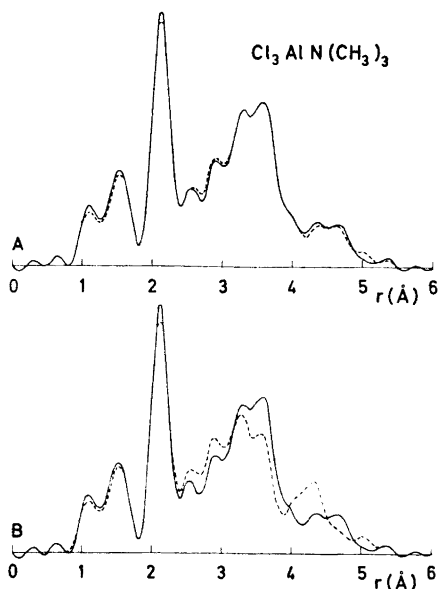


Fig. 1. A. Full line: Experimental radial distribution curve for $\text{Cl}_3\text{AlNMe}_3$. Stippled line: Theoretical radial distribution curve calculated for model in which the Cl atoms of the acceptor and Me groups of the donor are staggered with respect to rotation about the Al-N bond. B. Full line: Experimental radial distribution curve. Stippled line: Theoretical radial distribution curve calculated for model in which the Cl atoms of the acceptor and Me groups of the donor are eclipsed with respect to rotation about the Al-N bond. Artificial damping constant, $b=0.0025$ Å².

probably reflects the increasing stability of these complexes with increasingly electronegative substituents in the Al atom.

With the exception of the Al-N bond distance, the structure parameters obtained in this study are more accurate than those obtained by X-ray crystallography.

The N-C bonds in the complexes X_3AlNMe_3 are longer than the N-C bond in free trimethylamine, and appears to increase in length with increasing stability of the complexes: The N-C bond in $\text{Cl}_3\text{AlNMe}_3$ is significantly longer than the N-C bonds in H_3AlNMe_3 and $\text{Me}_3\text{AlNMe}_3$, 1.476(3) Å and 1.474(3) Å, respectively, and these bonds in turn are significantly

longer than the N–C bond in free NMe₃, 1.454(2) Å.

The \angle Al–N–C angle in Cl₃AlNMe₃ is larger than the corresponding angles in H₃AlNMe₃ and Me₃AlNMe₃, 109.0(0.3)° and 109.3(0.4)°, respectively, although the difference is of marginal statistical significance. Such a difference might easily be explained as the result of increased steric interaction between donor and acceptor due to the shortening of the Al–N bond.

The Al–Cl bond distance is in excellent agreement with the mean Al–Cl bond distance found in the crystal, 2.123 Å. Just as the N–C bond distances in the complexes X₃AlNMe₃ are longer than in free NMe₃ and appear to increase in length with increasing acceptor strength of X₃Al, so the Al–Cl bond distances in complexes of the type Cl₃Al–L are longer than the Al–Cl bond in free AlCl₃ and appear to increase with increasing donor strength of the base L: The Al–Cl bond in Cl₃AlNMe₃ is significantly longer than the mean Al–Cl bond distance in the complex of AlCl₃ with propionyl chloride,⁹ 2.093(3) Å, which in turn is significantly longer than the Al–Cl bond in free AlCl₃, 2.06 ± 0.01 Å.⁹

The shrinkage of the Cl...C(*trans*) distance was found to be 0.12(6) Å.

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Preparations of *trans*-Bis(2-picolylamine) Complexes of Chromium(III)

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In a recent paper,¹ two series of octahedral *cis*-bis(2-picolylamine) complexes of chromium were described (2-picolylamine = 2-aminomethylpyridine). The ligands in the *cis*-positions were Cl⁻, Br⁻, and H₂O. This paper reports the preparation of a series of the corresponding *trans*-complexes.

Only one type of geometrical isomer occurs, probably a *trans,trans,trans* isomer (Fig. 1. a). It is likely that the other imaginable isomer, the *trans,cis,cis* (Fig. 1 b), does not exist because of sterical hindrance.

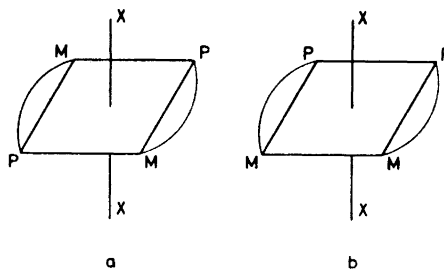


Fig. 1. The geometrical isomers of the *trans*-[Cr(C₆H₈N₂)₂X₂]ⁿ⁺ ion. P symbolizes the pyridine nitrogens, M, the methylamine nitrogens. a. The *trans,trans,trans* isomer. b. The *trans,cis,cis* isomer.

The preparations are based upon the reaction between the so-called α -*cis*-[Cr(C₆H₈N₂)₂Cl₂]Cl¹ and moist silver oxide. The resulting solution apparently contains both *trans*- and α -*cis*-[Cr(C₆H₈N₂)₂OH·H₂O]²⁺. By means of conc. nitric acid *trans*-[Cr(C₆H₈N₂)₂(H₂O)₂](NO₃)₃ is isolated from the reaction mixture and used as an initial material for *trans*-[Cr(C₆H₈N₂)₂Cl₂]Cl and *trans*-[Cr(C₆H₈N₂)₂Br₂]Br.

The assignment of geometric configuration is based entirely upon the colours of