

The Crystal and Molecular Structure of Trichlorotrimethylaminealuminum(III)

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The crystal and molecular structure of trichlorotrimethylaminealuminum(III) $[\text{AlCl}_3 \cdot \text{N}(\text{CH}_3)_3]$ has been determined by a three-dimensional X-ray analysis and is shown to be monomeric. The crystals are monoclinic with $a = 6.81 \pm 0.02$, $b = 10.66 \pm 0.03$, $c = 7.31 \pm 0.02$ Å; $\beta = 118^\circ 0' \pm 5'$; space group $P2_1$ with $Z = 2$. The aluminum–nitrogen distance is 1.96 Å.

Introduction

A large number of complexes of aluminum trichloride with Lewis bases have been described in the literature but in view of the importance of these compounds surprisingly few crystallographic studies have been made. Compounds of the type [aluminum trichloride, (ligand)] and [aluminum trichloride, 2(ligand)] have been extensively studied by other physical techniques, including vibrational spectroscopy. The spectra for the 1:1 adducts have generally been discussed in terms of simple monomeric four-coordinate aluminum structures, but agreement with solution molecular weight studies is by no means satisfactory. The molecular weight of trichlorotrimethylaminealuminum(III) $[\text{AlCl}_3 \cdot \text{N}(\text{CH}_3)_3]$, measured cryoscopically in benzene by Ruff (1961) gives a value between a monomer and a dimer, although the vibrational spectrum has been interpreted by Sawodny & Goubeau (1965) in terms of a monomer. More recent work by Beattie (1967) on the solid compound suggested that the Raman and infrared spectra were not unambiguous.

To resolve these uncertainties, at least in the solid state, a single-crystal X-ray structure determination was undertaken.

Experimental

The crystals of trichlorotrimethylaminealuminum(III) used were supplied by G. A. Ozin, Chemistry Department, University of Southampton, and were sealed in Pyrex glass capillary tubes under vacuum. A well formed crystal of approximate dimensions $0.2 \text{ mm} \times 0.2 \text{ mm} \times 0.5 \text{ mm}$ was mounted in its capillary tube on a standard goniometer head so that the crystal could be rotated about the b axis. Another crystal, mounted about the a axis, was used to obtain additional information to determine the space group and cell dimensions using oscillation and Weissenberg photographs. The crystallographic data are:

Monoclinic:

$$a = 6.81 \pm 0.02, \quad b = 10.66 \pm 0.03, \quad c = 7.31 \pm 0.02 \text{ \AA},$$

$$\beta = 118^\circ 0' \pm 5'.$$

$$d_o = 1.32 \pm 0.04 \text{ g.cm}^{-3}; \quad d_c = 1.34 \pm 0.02 \text{ g.cm}^{-3},$$

assuming two molecules of $[\text{AlCl}_3 \cdot \text{N}(\text{CH}_3)_3]$ per unit cell.

$$\mu = 9 \text{ cm}^{-1} \text{ for Mo } K\alpha.$$

Absent spectra are $0k0$ for k odd. The space group is thus either $P2_1$, with one molecule of $[\text{AlCl}_3 \cdot \text{N}(\text{CH}_3)_3]$ per asymmetric unit or $P2_1/m$ with half of this molecule related to the other half by the crystallographic mirror plane.

Equi-inclination data were collected on an Arndt and Phillips linear diffractometer for $k = 0 \rightarrow 10$ using a 30 sec oscillation motor and the balanced filter technique. The collection of data was limited to structure factors with $\sin \theta < 0.35$ due to thermal cut-off. The total number of reflexions recorded in this way was 730 and those with a net count less than 25 were considered, within the limits of this experiment, to be accidentally absent leaving 608 reflexions with non-zero weights. The data were reduced to structure factors by correcting for Lorentz and polarization effects in the usual way. No absorption corrections were made.

Structure determination

A three-dimensional unsharpened Patterson function showed only two peaks about 2 Å from the origin. These were identified as vectors between the aluminum atom and the chlorine atoms, one being a double peak due to vectors on either side of a mirror plane. The corresponding vectors between the chlorine atoms were also identified and the position of the aluminum trichloride part of the molecule was obtained by interpretation of the peaks in the body of the Patterson function. These coordinates satisfied the $P2_1/m$ space group. The aluminum atom and one of the chlorine atoms lay on the crystallographic mirror plane, the other chlorine atoms being mirrored on either side of this plane so that the aluminum trichloride part of the molecule formed a trigonal pyramid with the aluminum at the apex. A structure factor calculation based on these coordinates gave a reliability factor of 0.35. From the subsequent Fourier summation the positions of the nitrogen and carbon atoms were found, the trimethylamine group forming another trigonal pyramid about

the mirror plane and the nitrogen atoms appearing to be tetrahedrally coordinated to the aluminum. The remaining peaks in the Patterson function could be interpreted on the basis of this model.

Least-squares refinement using a Hughes weighting scheme and with isotropic temperature factors, reduced *R* to 0.18. A close inspection of the electron density round the position of one of the carbon atoms showed that the trimethylamine group did not conform to the space group *P*₂₁/*m*, the carbon peak being elongated perpendicular to the mirror plane. One of the carbon atoms was moved off its mirror position and, fixing the coordinates and thermal parameters of the aluminum and chlorine atoms, least-squares refinement with isotropic thermal parameters was continued in space group *P*₂₁. The trimethylamine group moved significantly from its previous position and *R* was reduced. Further refinement including all the atoms gave an *R* of 0.082. It was not possible to fix the hydrogen atoms from an electron density map and in view of the high thermal parameters on the carbon atoms this is not surprising.

It has been shown (Killean, 1967) on consideration of counting statistics alone that the correct weighting scheme for a constant-time experiment is not suitable for a satisfactory least-squares refinement and should

not be used. Modification can be made to this weighting scheme to take account of other random errors e.g. Shoemaker (1968); Grant, Killean & Lawrence (1968). In order to ensure that the small departure from

Table 1. Final coordinates and standard deviations

| | <i>x/a</i> | $\sigma(x/a)$ | <i>y/b</i> | $\sigma(y/b)$ | <i>z/c</i> | $\sigma(z/c)$ |
|-------|------------|---------------|------------|---------------|------------|---------------|
| Al | 0.1258 | 0.0004 | 0.2491 | 0.0005 | 0.3848 | 0.0004 |
| Cl(1) | 0.1922 | 0.0006 | 0.4110 | 0.0004 | 0.2574 | 0.0005 |
| Cl(2) | -0.2003 | 0.0004 | 0.2453 | 0.0010 | 0.3538 | 0.0005 |
| Cl(3) | 0.1904 | 0.0006 | 0.0811 | 0.0004 | 0.2609 | 0.0006 |
| N | 0.3309 | 0.0012 | 0.2472 | 0.0015 | 0.6822 | 0.0011 |
| C(1) | 0.5743 | 0.0017 | 0.2590 | 0.0015 | 0.7219 | 0.0020 |
| C(2) | 0.2570 | 0.0022 | 0.3596 | 0.0016 | 0.7763 | 0.0022 |
| C(3) | 0.3271 | 0.0017 | 0.1302 | 0.0015 | 0.7914 | 0.0021 |

Table 2. Final anisotropic temperature factors $\times 10^5$ defined as $\exp[-B_{ij}h_ih_j]$

| | <i>B</i> ₁₁ | <i>B</i> ₂₂ | <i>B</i> ₃₃ | <i>B</i> ₂₃ | <i>B</i> ₁₃ | <i>B</i> ₁₂ |
|-------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| Al | 4224 | 1030 | 2767 | -263 | 3447 | -1070 |
| Cl(1) | 7963 | 1385 | 4171 | 1589 | 6773 | 2368 |
| Cl(2) | 4150 | 2707 | 4453 | -238 | 4312 | -255 |
| Cl(3) | 6772 | 1265 | 5595 | -1533 | 5725 | -504 |
| N | 5190 | 938 | 3495 | -124 | 4597 | 757 |
| C(1) | 4444 | 1563 | 5089 | -153 | 4472 | 112 |
| C(2) | 6807 | 1727 | 4190 | -698 | 5071 | 2071 |
| C(3) | 3796 | 1863 | 4168 | 2511 | 3110 | -200 |

Table 3. Final structure factor calculation using parameters from Tables 1 and 2

| | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|-------|---------|-----------|---------|---------|---------|-----------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|---------|
| 0 0 1 | 2 38 41 | 3 186 183 | 4 18 28 | 5 57 65 | 6 29 33 | 7 187 178 | 8 0 66 | 9 0 64 | 10 1 1 | 11 1 1 | 12 1 1 | 13 1 1 | 14 1 1 | 15 1 1 | 16 1 1 | 17 1 1 | 18 1 1 | 19 1 1 | 20 1 1 | 21 1 1 | 22 1 1 | 23 1 1 | 24 1 1 | 25 1 1 | 26 1 1 | 27 1 1 | 28 1 1 | 29 1 1 | 30 1 1 | 31 1 1 | 32 1 1 | 33 1 1 | 34 1 1 | 35 1 1 | 36 1 1 | 37 1 1 | 38 1 1 | 39 1 1 | 40 1 1 | 41 1 1 | 42 1 1 | 43 1 1 | 44 1 1 | 45 1 1 | 46 1 1 | 47 1 1 | 48 1 1 | 49 1 1 | 50 1 1 | 51 1 1 | 52 1 1 | 53 1 1 | 54 1 1 | 55 1 1 | 56 1 1 | 57 1 1 | 58 1 1 | 59 1 1 | 60 1 1 | 61 1 1 | 62 1 1 | 63 1 1 | 64 1 1 | 65 1 1 | 66 1 1 | 67 1 1 | 68 1 1 | 69 1 1 | 70 1 1 | 71 1 1 | 72 1 1 | 73 1 1 | 74 1 1 | 75 1 1 | 76 1 1 | 77 1 1 | 78 1 1 | 79 1 1 | 80 1 1 | 81 1 1 | 82 1 1 | 83 1 1 | 84 1 1 | 85 1 1 | 86 1 1 | 87 1 1 | 88 1 1 | 89 1 1 | 90 1 1 | 91 1 1 | 92 1 1 | 93 1 1 | 94 1 1 | 95 1 1 | 96 1 1 | 97 1 1 | 98 1 1 | 99 1 1 | 100 1 1 |
|-------|---------|-----------|---------|---------|---------|-----------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|---------|

space group $P2_1/m$ was not a result of the weighting scheme used in the refinement it was decided to re-refine the structure in both space groups with the modified weighting scheme. The R index for space group $P2_1/m$

was reduced from 0.18 to 0.086 but with $\frac{\sum w\Delta^2}{m-n} = 1.46$;

however that for space group $P2_1$ was reduced to 0.078 with $\frac{\sum w\Delta^2}{m-n} = 1.04$. Clearly the structure in space

group $P2_1$ is to be preferred. The application of the weighting scheme to this structure is fully described elsewhere (Grant, Killean & Lawrence, 1969).

Table 1 gives the final coordinates and their standard deviations, Table 2 the anisotropic thermal parameters and Table 3 the structure factors.

Description of the structure

The bond lengths and bond angles with their standard deviations are listed in Tables 4 and 5. Fig. 1 shows a view of the structure projected down the b axis. There are no short intermolecular contacts. The heavy atoms are almost mirrored, within ten standard deviations, in a plane perpendicular to the b axis. The light atoms

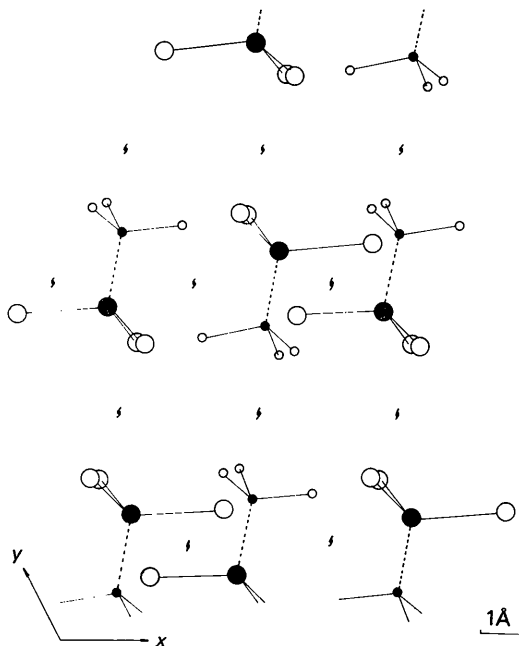


Fig. 1. Projection of the structure down the b axis.

are coordinated to the aluminum atom through the nitrogen atom in a tetrahedral arrangement with an aluminum–nitrogen distance of 1.96 Å. Viewed along this bond the aluminum–chlorine bonds approximately bisect the angles between the nitrogen–methyl bonds.

Table 4. Bond lengths and standard deviations based on coordinates from Table 1

| Bond | Length | Standard deviation |
|----------|--------|--------------------|
| Al–Cl(1) | 2.11 Å | 0.01 Å |
| Al–Cl(2) | 2.12 | 0.01 |
| Al–Cl(3) | 2.14 | 0.01 |
| Al–N | 1.96 | 0.01 |
| N–C(1) | 1.55 | 0.02 |
| N–C(2) | 1.58 | 0.02 |
| N–C(3) | 1.49 | 0.02 |

Table 5. Intramolecular bond angles and standard deviations

| | Angle | Standard deviation |
|----------------|--------|--------------------|
| Cl(1)–Al–Cl(2) | 113.5° | 0.4° |
| Cl(1)–Al–Cl(3) | 111.6 | 0.2 |
| Cl(1)–Al–N | 108.1 | 0.5 |
| Cl(2)–Al–Cl(3) | 110.5 | 0.4 |
| Cl(2)–Al–N | 106.5 | 0.3 |
| Cl(3)–Al–N | 106.3 | 0.5 |
| Al–N–C(1) | 110.5 | 0.7 |
| Al–N–C(2) | 105.6 | 1.0 |
| Al–N–C(3) | 114.9 | 1.1 |
| C(1)–N–C(2) | 113.0 | 1.2 |
| C(1)–N–C(3) | 104.7 | 1.1 |
| C(2)–N–C(3) | 108.3 | 0.8 |

Conclusions

The structure of trichlorotrimethylaminealuminum(III) has been shown to be monomeric in the solid state. The mean aluminum–chloride bond of 2.12 Å is similar to those found by Baenziger (1951) in $[\text{Na}]^+[\text{AlCl}_4]^-$. The aluminum is coordinated to the nitrogen atom of the trimethylamine in a tetrahedral arrangement and with a coordination distance of 1.96 Å.

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