Hydrogen Bond Studies XVIII.* The Crystal Structure of Trimethylammonium Chloride

By Jan Lindgren and Ivar Olovsson

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

The crystal structure of trimethylammonium chloride, $(CH_3)_3NHCl$, has been determined from three-dimensional single-crystal X-ray data obtained at room temperature. The crystals are monoclinic, space group $P2_1/m$, with two formula units in the cell of dimensions $a=6\cdot088$, $b=7\cdot033$, $c=7\cdot031$ Å and $\beta=95\cdot73°$. The structure contains uncharged units $(CH_3)_3NHCl$ composed of one trimethylammonium ion hydrogen bonded to a chloride ion (N–H$\cdots$Cl distance $3\cdot00$ Å). The N–H$\cdots$X bond length variation in ammonium and alkylammonium halides with the formulae NH_4X, RNH_3X, R_2NH_2X and R_3NHX is discussed.

Introduction

In the series of substituted ammonium chlorides where one or more hydrogen atoms in ammonium are replaced by methyl groups, the crystal structure of mono-methylammonium chloride has been determined by Hughes & Lipscomb (1946) and that of dimethyl-ammonium chloride by Lindgren & Olovsson (1968). In both cases X-ray diffraction techniques were used. Infrared spectra of the mono-, di- and trimethyl-ammonium chlorides have been reported by Bellanato (1960) who found strong hydrogen bonds in all three compounds.

In the present investigation the crystal structure of trimethylammonium chloride has been determined from single crystal X-ray diffraction data obtained at 20°C.

Experimental

Commercial trimethylammonium chloride was recrystallized several times from ethanol. Active carbon was used in the first recrystallizations to remove some coloured impurities. The salt was then dissolved in methanol, and ethyl ether was added until small needle-like crystals were obtained. As the crystals were somewhat hygroscopic they were sealed in thin-walled glass capillaries. A crystallographic axis was found to be parallel to the capillary axis as expected from the needle-like shape. With this, the c axis, as rotation axis layers $0 \leq l \leq 6$, were recorded using Ni-filtered Cu $K\alpha$ radiation and employing the equi-inclination Weissenberg method. The number of independent reflexions recorded was 606 but the intensities of 155 of these were too weak to be measured. The relative intensities were measured visually, employing the multiple-film technique (5 films) and comparison with an intensity scale. The data were corrected for the Lorentz and polarization effects. As the crystal corresponded very closely to a cylindrical specimen rotated around the cylinder axis an absorption correction could be easily applied with the use of standard programs. The linear absorp-

---

* Part XVII: *Acta Cryst.* (1968), B**24**, 549.

tion coefficient is $44\cdot6$ cm^{-1}; $r=0\cdot012$ cm. These corrections were calculated with the program ERLPA (Van den Hende, 1962).

Unit cell and space group

The diffraction symmetry $2/m$, with systematic absences $0k0$ with k odd suggests either the non-centrosymmetric space group $P2_1$ or the centrosymmetric $P2_1/m$. The structure is, as will be shown below, appropriately described in terms of the space group $P2_1/m$ (no. 11, *International Tables for X-ray Crystallography*, 1952).

Approximate cell dimensions were determined from rotation and Weissenberg photographs. More accurate values were subsequently obtained from a Guinier powder photograph, taken with strictly monochromatized Cu $K\alpha_1$ radiation (λCu $K\alpha_1 = 1\cdot54051$ Å), employing silicon as an internal standard ($a_{Si} = 5\cdot43054$ Å at 25°C). Using 42 powder reflexions thus recorded the most probable cell parameters were calculated by the least-squares method. The cell parameters together with their estimated standard deviations are: $a=6\cdot088 \pm 0\cdot003$, $b=7\cdot033 \pm 0\cdot002$, $c=7\cdot031 \pm 0\cdot002$ Å and $\beta= 95\cdot73 \pm 0\cdot04°$. The density of the crystal was approximately measured, using the method of flotation, as $1\cdot13 \pm 0\cdot05$ g.cm^{-3}. With two formula units in the cell the calculated density is $1\cdot060$ g.cm^{-3}.

Determination of the crystal structure

The positions of the chlorine atoms were derived from a three-dimensional Patterson synthesis. The interpretation was then based on the centrosymmetric space group $P2_1/m$. The nitrogen and carbon atoms were readily found from a Fourier synthesis based on the chlorine positions. In the structure thus obtained one carbon atom occupies a general fourfold position while the other carbon atom as well as the chlorine and nitrogen atoms occupy twofold positions (2*e*).

After a few cycles of least-squares refinements with individual isotropic temperature factors the R value, $R = \Sigma \, ||F_o| - |F_c||/\Sigma \, |F_o|$, was $13\cdot6\%$. At this stage a

difference synthesis was calculated to determine the hydrogen positions. For a further discussion of this point, see below. The hydrogen atoms thus determined were introduced in the refinements with fixed parameters; their isotropic temperature factors were set to 6 Å². The R value now dropped to 11·2%. The previous difference synthesis had indicated considerable anisotropy and an anisotropic refinement was therefore performed. An over-all scale factor was now refined (the inter-layer scaling was based on the previously obtained individual scale factors) while the parameters of the hydrogen atoms were fixed as before. In total the number of parameters refined increased from 20 in the isotropic case to 28 in the anisotropic case. The final R value after 3 cycles was 6·4%.

The structure was also refined in $P2_1$, starting with the preliminary coordinates derived from the Patterson synthesis but with the atoms shifted somewhat from the centrosymmetric positions. A significance test was made on the R-factor ratio as described by Hamilton (1965) with the hypothesis that the linear restrictions imposed on some parameters in $P2_1$ when using $P2_1/m$ are correct. The obtained ratio after final anisotropic refinements is 1·020. According to Hamilton's table the hypothesis cannot be rejected even at the 25% level. The space group $P2_1/m$ is therefore considered to be the best choice. The differences in the final atomic coordinates and interatomic distances in the two groups are within one standard deviation obtained with $P2_1$.

The function minimized in the refinements was $\Sigma w(|F_o| - |F_c|)^2$. The weighting function was that suggested by Cruickshank, Pilling, Bujosa, Lovell & Truter (1961), namely $w = 1/(a + |F_o| + c|F_o|^2)$, in which the final values for the constants were $a = 1·5$ and $c = 0·04$. Reflexions too weak to be measured were given zero weight. The scattering factors used were those for Cl^-, N^0, C^0 and H^0 listed in *International Tables for X-ray Crystallography* (1962, p. 202).
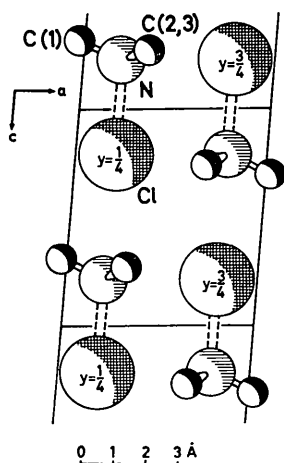
Fig. 1. View of the structure along the b axis. The carbon atoms C(2) and C(3) are related to each other by the mirror plane at $y = \frac{1}{4}$.

The atomic parameters with standard deviations obtained with $P2_1/m$ are listed in Table 1 and the distances and angles with standard deviations in Table 2. The distances given are not corrected for thermal motion since no experimental scaling has been done. Structure factors are compared in Table 3.

Table 1. *Atomic parameters with standard deviations* ($\times 10^4$)

The form of the anisotropic temperature factor is:
$$\exp\left[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)\right].$$
The r.m.s. components (R_i) of thermal displacement of the atoms along the ellipsoid axes are also listed (Å $\times 10^3$).

	Chlorine	Nitrogen	Carbon(1)	Carbon(2)
x	2095 (3)	2017 (9)	252 (10)	3187 (10)
y	25	25	75	4253 (9)
z	2136 (2)	7857 (7)	3065 (10)	7342 (9)
b_{11}	492 (7)	344 (2)	363 (24)	525 (21)
b_{22}	239 (3)	247 (11)	281 (15)	351 (14)
b_{33}	274 (5)	265 (12)	388 (18)	413 (13)
b_{12}	0	0	0	−152 (14)
b_{13}	78 (3)	60 (9)	78 (15)	63 (12)
b_{23}	0	0	0	−11 (12)
R_1	245 (2)	240 (5)	260 (5)	243 (6)
R_2	253 (2)	249 (5)	266 (7)	319 (5)
R_3	306 (2)	266 (5)	311 (7)	356 (7)

Table 2. *Distances and angles with standard deviations*

Distances

N–C(1)	1·466 (8) Å
N–C(2,3)	1·487 (7)
C(1)···C(2,3)	2·422 (8)
C(2)···C(3)	2·466 (12)
Cl···N	3·005 (5)
Cl···C(1)	3·791 (7)
Cl···C(2,3)	3·711 (6)
Cl···other nitrogen atoms	>4·0

Angles

C(1)–N–C(2,3)	110·2 (0·3)°
C(2)–N–C(3)	112·1 (0·6)
Cl···N–C(1)	111·3 (0·4)
Cl···N–C(2,3)	106·5 (0·3)

Crystallographic programs used in the structure determination: For the Fourier and Patterson calculations: STRIX and PROFFS (Liminga & Olovsson, 1964).

For the least-squares refinements: In the earlier stages SFLS (Åsbrink & Brändén, 1962) and in the later stages ORFLS (Busing, Martin & Levy, 1962). For calculation of the distances and angles: ORFFE (Busing, Martin & Levy, 1964).

Description and discussion of the structure

A view of the structure along the b axis is shown in Fig. 1. As seen the structure contains uncharged units, $(CH_3)_3NHCl$, composed of one trimethylammonium

ion hydrogen-bonded to a chloride ion. The N–H···Cl distance is 3·00 Å while the shortest distance between other nitrogen and chlorine atoms, not hydrogen-bonded to each other, is 4·03 Å. Accordingly only very weak attraction exists between adjacent units.

Bond distances and angles around nitrogen are shown in Fig. 2. The N–C bonds are 1·466 ± 0·008 and 1·487 ± 0·007 Å and the C–N–C angles 110·2 ± 0·3° and 112·1 ± 0·6°. The corresponding values for gaseous trimethylamine are 1·47 ± 0·02 Å and 108 ± 4° (Brockway & Jenkins, 1936). Accordingly there is no significant difference in the N–C bond lengths in these two compounds. The bond angles are, however, slightly smaller in trimethylamine than in trimethylammonium chloride. This may be expected from the well-known empirical rule that a lone pair exerts a stronger repulsion than a bonding pair.

Table 3. *Observed and calculated structure factors*

Reflexions too weak to be measured are marked with an asterisk and the values of $|F_o|$ given correspond to minimum observable intensities.

(The following is a large six-block table of structure factors. Each block has columns h, k, l, |F_o|, |F_c|.)

h	k	l	$|F_o|$	$|F_c|$
-1	0	0	13.6	13.3
-2	0	0	27.6	29.2
-3	0	0	3.7	3.5
-4	0	0	7.9	7.3
-5	0	0	5.8	5.6
-6	0	0	1.7*	1.6
-7	0	0	1.4*	1.5
-1	1	0	39.2	45.3
-2	1	0	6.0	6.3
-3	1	0	15.9	15.5
-4	1	0	9.5	9.8
-5	1	0	1.6*	0.4
-6	1	0	3.7	2.7
-7	1	0	1.4*	0.4
0	2	0	31.4	32.4
-1	2	0	20.5	21.5
-2	2	0	10.3	10.7
-3	2	0	12.3	11.3
-4	2	0	6.4	5.9
-5	2	0	8.1	7.8
-6	2	0	1.7*	0.3
-7	2	0	1.3	1.5
-1	3	0	14.6	14.9
-2	3	0	15.1	15.1
-3	3	0	9.9	9.5
-4	3	0	10.9	11.0
-5	3	0	1.7*	1.3
-6	3	0	2.4	2.6
-7	3	0	1.1*	0.3
0	4	0	19.8	19.6
-1	4	0	9.3	8.9
-2	4	0	10.8	9.4
-3	4	0	6.7	6.4
-4	4	0	5.7	6.4
-5	4	0	5.0	4.6
-6	4	0	1.5*	0.0
-1	5	0	12.7	13.4
-2	5	0	3.4	3.2
-3	5	0	6.9	6.5
-4	5	0	4.0	3.7
-5	5	0	1.6*	0.2
-6	5	0	1.2*	0.9
0	6	0	11.8	12.2
-1	6	0	2.8	2.4
-2	6	0	6.8	5.7
-3	6	0	1.7*	1.6
-4	6	0	2.4	1.9
-5	6	0	2.3	2.0
-1	7	0	5.5	5.2
-2	7	0	1.7*	1.7
-3	7	0	2.7	2.3
-4	7	0	2.6	2.4
0	8	0	3.6	3.6
-1	8	0	2.0	1.6
-2	8	0	1.9	1.7
-3	8	0	1.4*	1.7
4	0	1	5.1	5.8
3	0	1	5.6	5.5
2	0	1	26.5	24.9
1	0	1	1.5	0.4
-1	0	1	13.1	12.0
-2	0	1	8.2	8.0
-3	0	1	4.5	4.9
-4	0	1	4.0	4.6
-5	0	1	2.2	2.4
-6	0	1	1.3*	0.7
-7	0	1	1.5*	0.3
6	1	1	2.7	2.6
5	1	1	1.2*	0.1
4	1	1	11.0	11.6
3	1	1	8.5	8.1
2	1	1	6.5	7.0
-1	1	1	10.2	10.0
-2	1	1	20.9	20.1
-3	1	1	8.6	8.6
-4	1	1	3.7	4.2
-5	1	1	1.4*	1.4
-6	1	1	2.6	2.5
6	2	1	1.3*	1.1
5	2	1	1.5*	1.2
4	2	1	1.5*	0.9
3	2	1	1.3*	0.3
2	2	1	2.0	2.2
1	2	1	9.0	9.3
0	2	1	23.3	23.3
-1	2	1	6.8	6.3
-2	2	1	23.5	21.6
-3	2	1	6.5	6.3
-4	2	1	9.1	9.2
-5	2	1	1.2*	0.8
-6	2	1	2.9	2.8
-7	2	1	1.5*	1.3
6	3	1	1.2*	0.1
5	3	1	1.4*	0.8
4	3	1	1.5*	0.1
3	3	1	1.3*	0.6
2	3	1	2.3	2.3
1	3	1	10.2	10.8
0	3	1	0.9*	0.7
0	3	1	16.8	16.7

h	k	l	$|F_o|$	$|F_c|$
-1	3	1	14.0	13.8
-2	3	1	15.4	15.1
-3	3	1	1.1*	0.1
-4	3	1	1.3*	1.2
-5	3	1	1.5*	0.5
-6	3	1	1.5*	0.7
-7	3	1	1.0*	1.0
6	4	1	1.7	1.4
5	4	1	1.5*	0.0
4	4	1	1.3*	0.1
3	4	1	1.3*	0.1
2	4	1	4.9	4.9
1	4	1	8.1	8.5
0	4	1	3.4	3.0
-1	4	1	7.8	8.1
-2	4	1	2.6	2.4
-3	4	1	4.4	4.4
-4	4	1	1.4*	1.1
-5	4	1	1.5*	1.3
-6	4	1	1.3*	1.6
6	5	1	0.9*	0.1
5	5	1	1.4*	1.8
4	5	1	1.5*	0.6
3	5	1	5.5	5.1
2	5	1	2.7	2.7
1	5	1	2.8	2.8
0	5	1	2.3	1.9
-1	5	1	1.8	1.6
-2	5	1	5.8	6.0
-3	5	1	4.1	3.9
-4	5	1	1.5*	1.4
-5	5	1	1.0*	1.4
-6	5	1	1.0*	1.2
6	6	1	1.1*	0.7
5	6	1	2.0	2.0
4	6	1	1.5*	0.2
3	6	1	4.8	4.7
2	6	1	2.3	2.5
1	6	1	1.4*	1.2
0	6	1	2.9	2.8
-1	6	1	1.5*	1.8
-2	6	1	3.1	3.0
-3	6	1	1.5	1.8
-4	6	1	1.5	1.7
-5	6	1	1.1*	0.4
4	7	1	2.5	2.3
3	7	1	2.4	2.3
2	7	1	1.5*	1.4
1	7	1	2.4	2.1
0	7	1	1.4*	1.0
-1	7	1	3.5	3.7
-2	7	1	1.4*	1.4
-3	7	1	1.1*	1.3
3	8	1	0.9*	0.6
2	8	1	1.6	1.4
1	8	1	2.3	2.4
0	8	1	1.3*	0.7
-1	8	1	2.5	2.6
-2	8	1	1.1*	0.0
4	0	2	3.2	3.3
3	0	2	7.0	6.8
2	0	2	21.8	20.5
1	0	2	13.2	14.0
-1	0	2	23.0	20.8
-2	0	2	0.8*	0.7
-3	0	2	6.8	7.1
-4	0	2	4.8	5.3
-5	0	2	1.2*	1.1
-6	0	2	1.0	1.3
-7	0	2	1.7	1.6
4	1	2	1.2*	1.8
3	1	2	11.7	10.5
2	1	2	5.8	6.0
1	1	2	21.5	21.3
-1	1	2	17.4	12.7
-2	1	2	32.4	35.1
-3	1	2	10.8	10.7
-4	1	2	5.3	5.8
-5	1	2	1.8	1.6
-6	1	2	2.9	3.0
-7	1	2	1.2*	0.3
5	2	2	1.8	2.0
4	2	2	10.0	9.9
3	2	2	7.3	6.6
2	2	2	14.2	13.1
1	2	2	20.0	20.0
-1	2	2	3.4	3.0
-2	2	2	11.5	11.5
-3	2	2	7.6	6.9
-4	2	2	6.7	7.2
-5	2	2	5.9	6.6
-6	2	2	1.2*	0.1
-7	2	2	0.9	1.2
6	3	2	1.9	1.7
5	3	2	1.2*	0.3

h	k	l	$|F_o|$	$|F_c|$
3	3	2	9.2	8.8
2	3	2	4.9	5.0
1	3	2	9.8	9.0
0	3	2	7.0	7.2
-1	3	2	4.7	4.9
-2	3	2	15.5	15.4
-3	3	2	12.1	11.6
-4	3	2	8.3	8.7
-5	3	2	6.5	7.0
-6	3	2	2.9	2.9
-7	3	2	2.6	2.5
6	4	2	0.8*	0.4
5	4	2	0.9*	0.0
4	4	2	3.0	3.0
3	4	2	2.4	2.2
2	4	2	7.0	6.5
1	4	2	6.0	6.1
0	4	2	7.0	7.7
-1	4	2	13.0	13.3
-2	4	2	3.7	3.2
-3	4	2	9.5	9.2
-4	4	2	3.7	3.7
-5	4	2	6.0	6.1
-6	4	2	3.7	3.9
6	5	2	1.0*	0.2
5	5	2	0.6	0.5
4	5	2	1.0*	0.4
3	5	2	2.9	2.9
2	5	2	5.0	4.6
1	5	2	3.4	3.7
0	5	2	7.6	8.2
-1	5	2	12.2	11.9
-2	5	2	1.3	1.5
-3	5	2	5.1	5.3
-4	5	2	1.7	2.0
-5	5	2	1.1	1.1
-6	5	2	1.0	1.1
5	6	2	1.1*	0.7
4	6	2	2.2	2.2
3	6	2	4.1	4.1
2	6	2	3.3	3.4
1	6	2	8.5	9.0
0	6	2	1.2*	0.3
-1	6	2	5.5	5.2
-2	6	2	1.2*	0.4
-3	6	2	2.4	2.3
-4	6	2	1.8	1.9
5	7	2	2.0	2.0
4	7	2	1.9	1.9
3	7	2	1.6	1.7
2	7	2	3.6	3.2
1	7	2	1.2*	1.8
0	7	2	5.1	4.9
-1	7	2	1.2*	0.9
-2	7	2	3.2	3.2
-3	7	2	1.5	1.5
5	8	2	1.4	1.4
4	8	2	0.8*	1.0
3	8	2	1.4	1.6
2	8	2	2.7	2.8
1	8	2	0.9*	1.1
0	8	2	1.7	1.9
-1	8	2	3.6	3.2
-2	8	2	1.1	1.0
5	0	3	4.3	4.3
4	0	3	16.8	16.4
3	0	3	1.3	1.6
2	0	3	2.1	2.3
-1	0	3	2.8	3.0
-2	0	3	12.0	11.8
-3	0	3	2.4	2.3
-4	0	3	5.1	5.3
-5	0	3	1.1*	0.1
-6	0	3	0.7*	0.7
5	1	3	2.7	2.3
4	1	3	1.3	1.7
3	1	3	0.9	0.8
2	1	3	0.9*	0.8
1	1	3	14.6	13.1
0	1	3	12.3	12.2
-1	1	3	14.1	14.5
-2	1	3	1.2	0.8
-3	1	3	1.4	1.4
-4	1	3	3.5	3.4
-5	1	3	1.1*	1.2
-6	1	3	1.3*	0.6
5	2	3	1.5*	0.7
4	2	3	1.4	1.5
3	2	3	11.0	11.0
2	2	3	9.5	9.7
1	2	3	10.6	10.2
0	2	3	12.7	11.9
-1	2	3	10.3	10.4
-2	2	3	9.9	10.8
-3	2	3	1.3*	0.6

h	k	l	$|F_o|$	$|F_c|$
-5	2	3	3.4	3.6
-6	2	3	1.5*	0.7
-7	2	3	1.0*	0.7
6	3	3	1.1*	1.3
5	3	3	1.5*	0.7
3	3	3	3.5	3.7
2	3	3	2.8	2.8
1	3	3	11.9	12.4
0	3	3	11.6	11.3
-1	3	3	3.3	3.4
-2	3	3	3.3	3.6
-3	3	3	1.5*	0.6
-4	3	3	0.9*	0.7
-5	3	3	1.3*	1.0
5	4	3	2.0	2.1
4	4	3	1.5	1.2
3	4	3	2.0	2.1
2	4	3	6.3	6.4
1	4	3	4.4	4.5
0	4	3	5.4	6.2
-1	4	3	5.2	5.6
-2	4	3	5.4	6.0
-3	4	3	6.2	6.3
-4	4	3	1.5*	0.9
-5	4	3	2.1	2.2
-6	4	3	1.2*	1.0
5	5	3	1.5	1.4
4	5	3	3.7	3.7
3	5	3	1.5*	0.4
2	5	3	5.1	5.3
1	5	3	2.3	2.1
0	5	3	3.7	4.1
-1	5	3	5.5	5.5
-2	5	3	3.0	2.9
-3	5	3	1.3*	0.7
-4	5	3	1.6	1.8
-5	5	3	1.6	1.5
5	6	3	1.4*	1.3
4	6	3	4.5	4.5
3	6	3	1.5*	1.2
2	6	3	2.7	2.9
1	6	3	2.0	2.2
0	6	3	1.3	1.3
-1	6	3	4.0	4.0
-2	6	3	2.0	2.0
-3	6	3	2.0	1.9
5	7	3	1.3*	0.4
4	7	3	1.3	1.3
3	7	3	3.0	2.8
2	7	3	2.3	2.3
1	7	3	3.4	3.3
0	7	3	1.2*	1.0
-1	7	3	1.7	1.8
-2	7	3	1.7	1.4
4	8	3	1.8	1.5
3	8	3	2.0	1.9
0	0	5	5.3	7.8
1	0	5	1.6	1.4
-2	0	5	7.5	5.9
-3	0	5	0.9*	0.0
-4	0	5	4.8	4.3
-5	0	5	0.8*	0.3
-6	0	5	0.4*	1.0
4	1	5	0.8*	1.2
3	1	5	4.1	3.7
2	1	5	9.6	9.0
1	1	5	1.0	1.0
0	1	5	9.8	8.5
-1	1	5	7.5	6.6
-2	1	5	6.0	5.7
-3	1	5	2.9	2.9
-4	1	5	6.0	5.7
-5	1	5	0.9*	0.3
-6	1	5	0.9*	1.1
5	2	5	0.7*	0.4
4	2	5	2.2	1.9
3	2	5	5.3	5.5
2	2	5	1.9	1.9
1	2	5	7.1	7.2
0	2	5	7.7	6.7
-1	2	5	1.9	1.4
-2	2	5	6.8	6.8
-3	2	5	5.0	5.3
-4	2	5	3.0	3.1

h	k	l	$|F_o|$	$|F_c|$
-6	2	4	1.0	0.8
-7	2	4	0.6*	0.6
6	3	4	1.0*	0.6
5	3	4	4.9	4.4
4	3	4	1.1*	1.0
3	3	4	5.0	5.2
2	3	4	1.2	1.6
1	3	4	5.7	5.7
0	3	4	7.4	7.5
-1	3	4	3.2	3.5
-2	3	4	4.9	5.3
-3	3	4	2.3	2.3
-4	3	4	3.4	3.1
-5	3	4	1.3	1.5
5	4	4	1.1	1.2
4	4	4	1.1*	0.0
3	4	4	2.0	2.1
2	4	4	4.9	5.0
1	4	4	4.7	5.1
0	4	4	1.6	1.6
-1	4	4	5.7	5.8
-2	4	4	0.6*	0.5
-3	4	4	4.4	4.3
-4	4	4	1.5	1.7
-5	4	4	0.8*	0.5
-6	4	4	1.8	1.8
5	5	4	1.8	1.6
4	5	4	4.4	4.2
3	5	4	2.0	2.1
2	5	4	4.9	5.0
1	5	4	3.0	3.0
0	5	4	4.5	6.5
-1	5	4	6.0	6.5
-2	5	4	0.8	0.8
-3	5	4	3.5	3.3
-4	5	4	1.1*	0.0
5	6	4	1.1	1.3
4	6	4	0.7*	0.2
3	6	4	1.7	1.6
2	6	4	1.8	1.7
1	6	4	2.6	2.6
0	6	4	4.0	4.0
-1	6	4	1.8	1.9
-2	6	4	3.4	3.3
-3	6	4	1.1*	0.6
5	7	4	0.6*	0.4
4	7	4	1.2	1.2
3	7	4	1.9	2.0
2	7	4	2.8	2.8
1	7	4	0.9*	0.2
0	7	4	1.4	1.4
-1	7	4	0.8	1.2
4	0	5	2.3	2.3
3	0	5	3.9	4.4

h	k	l	$|F_o|$	$|F_c|$
-5	3	5	0.9*	0.7
-6	3	5	1.4	1.7
3	4	5	2.1	2.0
2	4	5	4.2	4.2
1	4	5	0.9*	0.9
0	4	5	5.3	5.4
-2	4	5	5.8	5.6
-3	4	5	5.0	4.5
-4	4	5	0.9*	0.5
-5	4	5	1.9	2.0
3	5	5	1.9	1.8
2	5	5	1.7	1.6
1	5	5	4.2	4.2
-1	5	5	3.9	3.7
-2	5	5	3.1	2.9
-4	5	5	2.9	2.7
3	6	5	1.1	1.3
2	6	5	2.6	2.8
1	6	5	0.9*	0.2
0	6	5	2.7	2.7
-2	6	5	0.9	0.9
-3	6	5	3.2	2.9
-4	6	5	0.6*	0.1
2	7	5	2.1	2.3
1	7	5	1.9	2.1
-2	7	5	1.6	1.8
3	0	6	1.7	1.5
2	0	6	1.4	1.5
1	0	6	3.2	3.3
0	0	6	2.0	2.8
-1	0	6	2.5	5.1
-2	0	6	2.5	3.6
-4	0	6	3.1	2.8
-5	0	6	0.5*	0.1
3	1	6	0.3*	0.0
1	1	6	0.5*	0.0
2	1	6	2.0	2.0
1	2	6	0.4	0.4
0	1	6	4.5	5.1
-1	1	6	4.4	3.8
-2	1	6	2.6	2.6
-3	1	6	3.5	2.0
-4	1	6	1.2	1.3
-5	1	6	0.4	0.5
-6	1	6	1.0	1.0
3	2	6	0.6	0.7
2	2	6	2.4	2.3
1	2	6	2.1	2.1
0	2	6	3.2	3.1
-1	3	6	2.1	2.0
-3	3	6	2.2	2.6
-4	4	6	2.5	2.4
-2	4	6	2.5	2.2
-3	4	6	0.3*	0.0
-5	5	6	1.4*	1.3
-3	5	6	2.0	1.9
-3	5	6	1.2	1.2
-2	6	6	0.3	0.7
0	6	6	1.8	0.8
-2	6	6	1.3	1.2
-3	6	6	0.7	0.9

Hydrogen

The difference map calculated before the anisotropic refinement (see above) was used to locate the hydrogen atoms.

The hydrogen atom connecting the nitrogen and chlorine atoms was placed on the line joining the atoms at 1·03 Å from the nitrogen atom. This position was clearly indicated in the difference map by a peak which was, however, rather smeared out. The coordinates used were (0·205, 0·25, −0·065). The positions of the hydrogen atoms of the methyl groups were easily obtained as only three peaks (within reasonable distances from the carbon atoms) were found around each carbon atom. Naturally, one cannot expect to derive these positions accurately from the available X-ray data. The hydrogen atoms were accordingly located within the experimental peaks but with the coordinates adjusted to a C–H bond length of 1·1 Å and a H–C–H angle of 109·5°. The hydrogen positions correspond to a staggered configuration of the methyl groups relative the bonds around the nitrogen atoms. The positions of the hydrogen atoms are illustrated in Fig. 3. As seen there are five independent hydrogen atoms with coordinates (−0·02, 0·25, −0·46), (−0·11, 0·37, −0·27), (0·24, 0·54, −0·23), (0·48, 0·43, −0·19) and (0·34, 0·43, −0·42).

Discussion of N–H · · · Cl *bond lengths*

In the ammonium and alkylammonium halides with the formulae NH$_4$X, RNH$_3$X, R$_2$NH$_2$X and R$_3$NHX, all hydrogen atoms around nitrogen are expected to be involved in hydrogen bonds. The only atom to accept such hydrogens in the above compounds is the negative ion X$^-$. One thus concludes that each halogen should be hydrogen-bonded to four, three, two and one nitrogen atom, respectively. Or expressed differently, the coordination number of halogen is expected to be equal to the number of hydrogen atoms around nitrogen, *i.e.* 4, 3, 2 and 1, respectively (*cf.* Tsoucaris, 1961).

In practice, it is found that complications sometimes arise because of orientational disorder or restricted rotation of the ammonium groups. Thus in NH$_4$Cl with the CsCl-*type* structure ammonium is surrounded by eight halogen neighbours at the corners of a cube. One particular ammonium directs its hydrogens towards four of these neighbours, but above the λ-point

(−30 °C) there is complete disorder between the two possible orientations of ammonium.

In methylammonium chloride, CH$_3$NH$_3$Cl, nitrogen is analogously surrounded not by three halogen atoms as expected but by four; one has here assumed restricted rotation or orientational disorder around the C–N bond (Hughes & Lipscomb, 1946).

In dimethylammonium chloride, (CH$_3$)$_2$NH$_2$Cl, each nitrogen atom is hydrogen-bonded to two chlorine atoms and each chlorine atom is hydrogen-bonded to two nitrogen atoms. In trimethylammonium chloride (CH$_3$)$_3$NHCl, each nitrogen atom is hydrogen-bonded to one chlorine atom, and each chlorine atom is hydrogen-bonded to one nitrogen atom. The last two structures thus conform with the general ideas above.

When comparing the N–H · · · Cl distances in these compounds several effects must be taken into consideration. Two of the most obvious and important ones are discussed below.

Firstly, when one or more hydrogen atoms in an ammonium ion are substituted by other groups, the N–H · · · Cl distance is expected to change depending on the difference in electronegativity between the substituents and hydrogen as discussed in a previous paper (Olovsson, 1960*a*). In the compounds now discussed hydrogen is substituted with methyl groups and essentially no change of the bond length is to be expected due to this substitution, since the electronegativities of hydrogen and a methyl group are probably quite comparable.

Secondly the coordination number of the atoms involved in the hydrogen bond must be considered. In the same way as in ordinary chemical bonds the bond length should increase with increasing coordination number. In this case the coordination number of both the hydrogen donor atom and the acceptor atom must be considered. Therefore the coordination numbers of nitrogen and chlorine will be discussed in some detail.

In NH$_4$Cl with the CsCl-*type* structure the coordination number of both nitrogen and chlorine is eight; the N–H · · · Cl distance is 3·35 Å. In NH$_4$Cl with the NaCl-*type* structure the coordination number of both is six; the N–H · · · Cl distance is here 3·26 Å.

In CH$_3$NH$_3$Cl the coordination number of nitrogen is five (one methyl group, to which it is covalently bonded, and four chlorine atoms). The coordination number of chlorine is four. The N–H · · · Cl distance

Table 4. *Coordination numbers of nitrogen and chlorine and* N–H · · · Cl *distances in the compounds discussed in the text*

	Coordination number of N	Coordination number of Cl	N–H · · · Cl distance
NH$_4$Cl (CsCl-type)	8	8	3·35 Å
NH$_4$Cl (NaCl-type)	6	6	3·26
NH$_4$Cl.3NH$_3$	4	1+11	3·22
CH$_3$NH$_3$Cl	5	4	3·18
(CH$_3$)$_2$NH$_2$Cl	4	2	3·11
(CH$_3$)$_3$NHCl	4	1	3·00

in this compound is 3·18 Å (Hughes & Lipscomb, 1946). Note, however, that in the three cases now discussed there is orientational disorder or restricted rotation of the ammonium groups (see above) such that the observed distances may be influenced by these effects.

In $NH_4Cl.3NH_3$ (Olovsson, 1960b), ammonium is surrounded by three ammonia molecules and one chlorine atom and the coordination number is thus four. Chlorine on the other hand is surrounded by one ammonium ion (distance 3·22 Å) and eleven ammonia molecules, which are, however, more distant (average distance 3·72 Å); the coordination number of chlorine is thus somewhat difficult to assign and is here written as 1+11.

In $(CH_3)_2NH_2Cl$ the N–H···Cl distance is 3·11 Å (Lindgren & Olovsson, 1968). The coordination number of nitrogen is four (two methyl groups, to which it is covalently bonded, and two chlorine atoms, to which it is hydrogen-bonded), while the coordination number of chlorine is two.

In $(CH_3)_3NHCl$ the N–H···Cl distance is 3·00 Å (present investigation). The coordination number of nitrogen is four (three methyl groups covalently bonded and one chlorine atom which is hydrogen-bonded) and the coordination number of chlorine is one.

The situation is summarized in Table 4.

One notices a continous decrease in the bond length N–H···Cl with the decrease of the coordination numbers. It is clear, however, that more compounds have to be investigated in order to determine the relative importance of the coordination numbers of the nitrogen and the chlorine atoms. The possible effect due to substitution of H by CH_3 (see above) must also be further investigated. Only a short remark on some infrared work will be made below.

In the series mono-, di-, and trimethylammonium chlorides Bellanato (1960) found a successive decrease in the N–H stretching frequencies. From the general relationship between the A–H stretching frequency and the bond distance A–H···B (Nakamoto, Margoshes & Rundle, 1955) a corresponding successive decrease is to be expected in the N–H···Cl distance on passing from the mono- to the trimethylammonium chloride. The distances in CH_3NH_3Cl, 3·18 Å (Hughes & Lipscomb, 1946) in $(CH_3)_2NH_2Cl$, 3·11 Å (Lindgren & Olovsson, 1968) and in $(CH_3)_3NHCl$, 3·00 Å (present work) thus follow the expected trend (cf. also Tsoucaris, 1961).
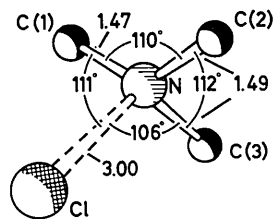
Fig. 2. Bond distances and angles around nitrogen.
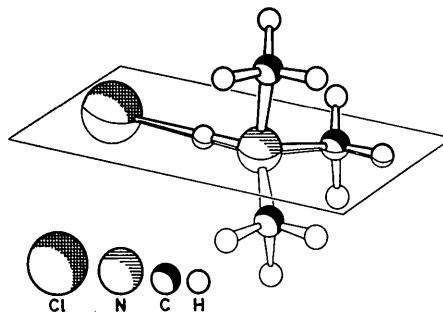

Fig. 3. The uncharged unit $(CH_3)_3NHCl$ showing the orientation of the methyl groups. The mirror plane perpendicular to the b axis is indicated.

References

BELLANATO, J. (1960). Spectrochim. Acta, 16, 1344.

BROCKWAY, L. O. & JENKINS, H. O. (1936). J. Amer. Chem. Soc. 58, 2036.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

CRUICKSHANK, D. W. J., PILLING, D. E., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). In Computing Methods and the Phase Problem in X-ray Crystal Analysis. Oxford: Pergamon Press.

HAMILTON, W. C. (1965). Acta Cryst. 18, 502.

HUGHES, E. W. & LIPSCOMB, W. N. (1946). J. Amer. Chem. Soc. 68, 1970.

International Tables for X-ray Crystallography (1952). Vol. I. Birmingham: Kynoch Press.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

LIMINGA, R. & OLOVSSON, I. (1964). Acta Polytech. Scand., Math. Computing Mach. Ser. No. 10.

LINDGREN, J. & OLOVSSON, I. (1968). Acta Cryst. B24, 549.

NAKAMOTO, K., MARGOSHES, M. & RUNDLE, R. E. (1955). J. Amer. Chem. Soc. 77, 6480.

OLOVSSON, I. (1960a). Ark. Kemi, 16, 437.

OLOVSSON, I. (1960b). Acta Chem. Scand. 14, 1453.

TSOUCARIS, G. (1961). Acta Cryst. 14, 917.

VAN DEN HENDE, J. H. (1962). Esso Research and Engineering Company CBRL-27M-62.

ÅSBRINK, S. & BRÄNDEN, C.-I. (1962). IUCr World List of Cryst. Computer Programs, no. 6023 Facit.