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Crystal Structure of Triaminoguanidinium Chloride, $(NH_2.NH)_3C.Cl$*

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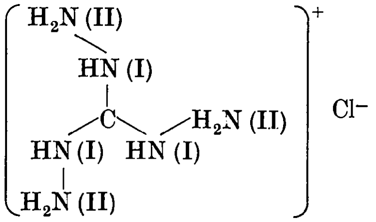
Triaminoguanidinium chloride crystallizes in the hexagonal system. Unit-cell dimensions are $a = 7{\cdot}528$, $c = 6{\cdot}253$ Å, and the space group is $P6_3/m$. The crystal structure was solved by standard methods and refined by least squares. The triaminoguanidinium ion is planar except for the positions of the hydrogen atoms, and C–N and N–N distances are $1{\cdot}31_8$ and $1{\cdot}45_0$ Å respectively. The ion possesses threefold symmetry. An N–H · · · Cl hydrogen bond distance of $3{\cdot}18_9$ Å is found from nitrogen atoms attached to the central carbon atom to the chlorine ion with the same *z* coordinate; a layer structure parallel to the (001) plane is thus formed. The nature of the triaminoguanidinium ion is discussed.

Introduction

Although guanidine is one of the more important organic bases, accurate interatomic distances have not been determined for the unsubstituted or symmetrically-substituted guanidinium ion. The discovery of ferroelectricity at room temperature in guanidinium aluminum sulfate hexahydrate and isomorphs by Holden, Matthias, Merz & Remeika (1956) led us to determine the structure of the chromium salt of this series (Pepinsky, Jona, Shirane & Okaya, 1956), and to compare it with the structure of the ferroelectric organic amine alums. The present study concerns the structure of the triaminoguanidinium ion in its chloride salt:



Crystal data

Triaminoguanidinium chloride crystallizes in the hexagonal system with

$$a = 7{\cdot}528,\quad c = 6{\cdot}253\ \text{Å}\,.$$

The observed density is 1·550 g.cm.$^{-3}$ at room temperature; the number of chemical units in the unit cell is two. Perfect cleavage was observed parallel to the plane (001). The Laue symmetry is C_{6h}; the only observed systematic absences are (00*l*) for *l* odd, which is consistent with space group $P6_3$ or $P6_3/m$.

Table 1. *Triaminoguanidinium chloride; observed and calculated structure factors*

(001) projection

h k i	$\|F_o\|$	F_c	$\|\Delta\|$	*h k i*	$\|F_o\|$	F_c	$\|\Delta\|$	*h k i*	$\|F_o\|$	F_c	$\|\Delta\|$
0 0 0	—	148·00	—	2 1 $\bar{3}$	10·96	−8·58	2·38	4 2 $\bar{6}$	2·22	−2·38	0·16
1 0 $\bar{1}$	21·50	22·38	0·88	2 2 $\bar{4}$	29·72	29·12	0·60	4 3 $\bar{7}$	3·28	−2·74	0·54
2 0 $\bar{2}$	26·90	−24·78	2·12	2 3 $\bar{5}$	12·08	−10·82	1·26	4 4 $\bar{8}$	8·40	8·64	0·24
3 0 $\bar{3}$	10·48	10·00	0·48	2 4 $\bar{6}$	7·20	−7·36	0·16	4 5 $\bar{9}$	3·84	−3·74	0·10
4 0 $\bar{4}$	11·10	−9·20	1·90	2 5 $\bar{7}$	8·10	8·88	0·78				
5 0 $\bar{5}$	11·38	10·36	1·02	2 6 $\bar{8}$	5·42	−5·44	0·02	5 1 $\bar{6}$	11·34	11·78	0·44
6 0 $\bar{6}$	19·70	21·62	1·92	2 7 $\bar{9}$	1·14	−1·56	0·42	5 2 $\bar{7}$	11·92	11·82	0·10
7 0 $\bar{7}$	2·54	−2·44	0·10					5 3 $\bar{8}$	4·48	−4·98	0·50
8 0 $\bar{8}$	2·76	−2·58	0·18	3 1 $\bar{4}$	11·64	−11·22	0·42	5 4 $\bar{9}$	4·86	−5·06	0·20
				3 2 $\bar{5}$	8·62	−9·38	0·76				
1 1 $\bar{2}$	28·50	28·94	0·44	3 3 $\bar{6}$	10·02	10·66	0·64	6 1 $\bar{7}$	0·78	1·58	0·80
1 2 $\bar{3}$	3·46	0·56	2·90	3 4 $\bar{7}$	0·00	1·02	1·02	6 2 $\bar{8}$	2·76	−1·94	0·82
1 3 $\bar{4}$	6·42	−6·02	0·40	3 5 $\bar{8}$	3·22	−3·30	0·08	6 3 $\bar{9}$	7·38	7·30	0·08
1 4 $\bar{5}$	12·08	11·68	0·40	3 6 $\bar{9}$	4·48	4·32	0·16				
1 5 $\bar{6}$	1·40	−2·02	0·62					7 1 $\bar{8}$	6·14	6·30	0·16
1 6 $\bar{7}$	3·70	−4·14	0·44	4 1 $\bar{5}$	27·48	22·40	5·08	7 2 $\bar{9}$	0·00	−0·10	0·10
1 7 $\bar{8}$	8·00	8·32	0·32								

$\Sigma|F_o| = 377{\cdot}40 \quad \Sigma|\Delta| = 32{\cdot}14 \quad R = 0{\cdot}085$

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If the space group is $P6_3/m$, the triaminoguanidinium ion possesses threefold symmetry and is planar except for the six hydrogen atoms attached to N(II) (amine) atoms; and these six hydrogens should be arranged in pairs mirrored across the plane of the ion. Moreover, the plane of the triaminoguanidinium ion should have the same z coordinate as the chlorine ion. Extremely strong and normally decreasing $(0,0,2n)$ reflections, and the close similarity in the distribution of intensities on c-axis Weissenberg photographs of the zeroth, second and fourth layers, plus similar relations between reflections in the first and third layers, led to the choice of $P6_3/m$. This choice was confirmed by the analysis.

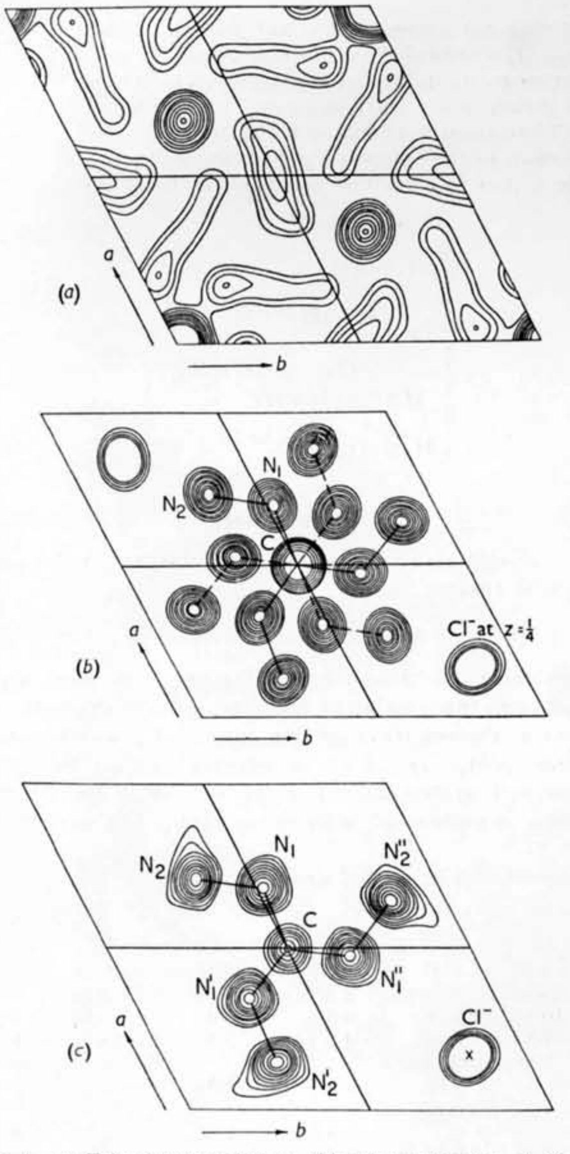

Fig. 1. (*a*) Triaminoguanidinium chloride: projection of Patterson function on (001). Origin at corner. (*b*) Triaminoguanidinium chloride: projection of electron density on (001). Molecule with full lines lies at $z = \frac{1}{4}$; molecule with broken lines lies at $z = \frac{3}{4}$. Origin at center. (*c*) Triaminoguanidinium chloride:

$$\int_0^1 \varrho(x, y, z)[1 + \sin 2\pi 1z]dz.$$

Atoms at $z = \frac{1}{4}$ appear. Origin at center.

Structure determination

The number of chemical units in the cell is two. General positions in $P6_3/m$ are twelvefold. Thus all the atoms in this structure are in special positions. Inspection of the Patterson function projected on (001), as shown in Fig. 1(*a*), and trial calculations of structure factors, led to the following set of coordinates (*International Tables*, 1952, p. 283):

2 C in (*a*) $\bar{6}$,	$(0, 0, \frac{1}{4};\ 0, 0, \frac{3}{4})$;
2 Cl in (*d*) $\bar{6}$,	$(\frac{1}{3}, \frac{2}{3}, \frac{3}{4};\ \frac{2}{3}, \frac{1}{3}, \frac{1}{4})$;
6 N(I) in (*h*) m,	$(x_1, y_1, \frac{1}{4};$ etc.);
6 N(II) in (*h*) m,	$(x_2, y_2, \frac{1}{4};$ etc.);

and similarly for hydrogen atoms.

The four parameters x_1, x_2, y_1 and y_2 were refined first by using repeated structure-factor and electron-density calculations for $(hk0)$ reflections. The final electron-density projection on (001) is shown in Fig. 1(*b*). At this stage the generalized electron density projection

$$\int_0^1 \varrho(x, y, z)[1 + \sin 2\pi 1z].dz$$

was calculated using $(hk0)$ and $(hk1)$, in order to show one triaminoguanidinium ion at $z = \frac{1}{4}$. This generalized projection is shown in Fig. 1(*c*). From these maps new parameters were selected which were corrected for series-termination errors in the usual manner. The disagreement factor $R = \Sigma||F_o|-|F_c|| \div \Sigma|F_o|$ at this stage was 0·12 and 0·13 for $(hk0)$ and $(hk1)$ respectively. A least-squares refinements of coordinates was carried out, and individual temperature factors were established for the (001) projection. In the course of these refinements

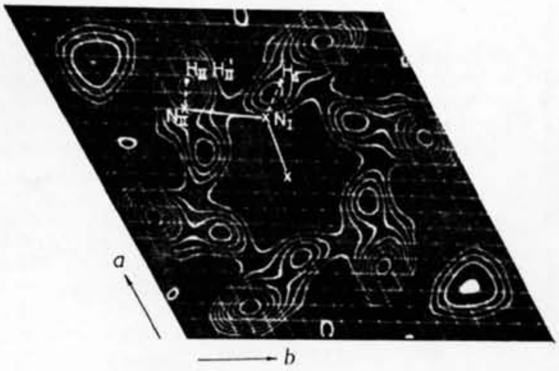

Fig. 2. Triaminoguanidinium chloride: final $F_o - F_c$ synthesis (F_c without hydrogens). Positions of carbon and nitrogen atoms are shown by crosses. Positive contours only.

the F_o's were corrected for secondary extinction, using the formula

$$F_o^{\text{corrected}} = F_o \exp\,(gF_c^2 \times LPF)$$

(all symbols have usual meanings), with $g = 5{\cdot}08 \times 10^{-5}$. Positions of hydrogen atoms, obtained from $(F_o - F_c)$ syntheses, were included in structure-factor calculations for low $\sin\theta$ reflections. The final disagreement factor is 0·085. In Table 1, observed and calculated structure factors are listed. Fig. 2 is the final $F_o - F_c$ (F_c without hydrogens) synthesis, with the other atoms marked for reference. In Table 2, the atomic coordinates and the individual temperature factors $B_{\parallel}$ in the (001) plane are listed. As the accuracy of coordinates of hydrogen atoms is low, these are not included in Table 2. Their approximate positions can be obtained from Fig. 2.

Table 2. *Triaminoguanidinium chloride: atomic coordinates and individual temperature factors (after least-square refinements)*

Atom	x	y	z	$B_{\parallel}$ (cm.^{2})
Cl	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{1}{4}$	$2{\cdot}26 \times 10^{-16}$
C	0	0	$\frac{1}{4}$	2·49
N_1	$0{\cdot}184_5$	$0{\cdot}020_5$	$\frac{1}{4}$	2·38
N_2	$0{\cdot}206_5$	$-0{\cdot}160_2$	$\frac{1}{4}$	2·38

$B_{\parallel}$ = temperature factors in (001) plane.

As is usual in crystals with planar molecules or ions forming layer structures, marked anisotropy was observed in the thermal motions of the atoms in this crystal; the temperature factor perpendicular to the plane (001), $B_{\perp}$, is much greater than $B_{\parallel}$. As the intensities of ($h0l$) reflections were slightly less reliable than those of ($hk0$) owing to the cleavage in the crystal, no attempt was made to obtain $B_{\perp}$ for individual atoms. An average $B_{\perp}$ was assigned as $3{\cdot}91 \times 10^{-16}$ cm.^{2}, from an F_o and F_c comparison for ($h0l$) with disagreement factor 0·12. This anisotropy in thermal motion is similar to that in the crystal of uracil (Parry, 1954), where $B_{\perp} - B_{\parallel}$ is about $2{\cdot}2 \times 10^{-16}$ cm.^{2}.

Bond distances and angles in triaminoguanidinium ion are shown in Fig. 3.

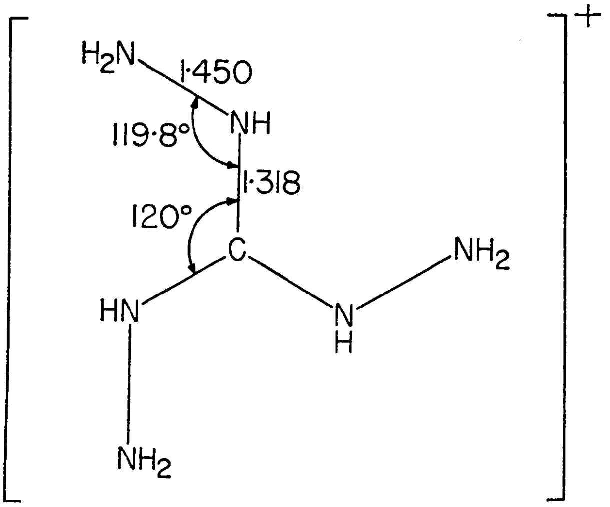

Fig. 3. Triaminoguanidinium ion: bond distances and angles. Symmetry = $\bar{6}$; planar.

Discussion of the structure

Triaminoguanidinium chloride has a typical layer structure. Hydrogen bonds are formed from each chloride ion to the three nearest N(I)'s at the same z coordinates, forming a two-dimensional N–H · · · Cl network along (001). The distances from a chlorine ion to any nitrogen atoms on the layers $\frac{1}{2}c$ apart are much larger than normal hydrogen-bond distances, and a cleavage parallel to (001) is therewith accounted for. A projection of the structure illustrating this feature is shown in Fig. 4. Coordination of nitrogen atoms around a chlorine ion is shown in Fig. 5. N(II) makes no hydrogen bond with a chlorine ion,

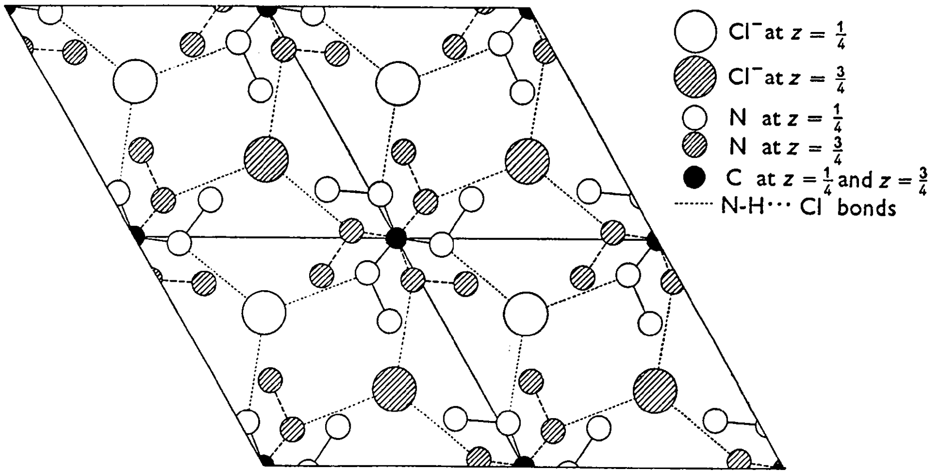

Fig. 4. Triaminoguanidinium chloride: projection of four cells on (001).

and this fact is involved in our discussion, below, of the resonance state of the triaminoguanidinium ion. The hydrogen bond of the distance $3\cdot18_9$ Å is normal for the N–H · · · Cl bond [compare 3·14–3·25 Å in cyclohexylamine hydrochloride (Shimada, Okaya & Nakamura, 1955); 3·11 and 3·18 Å in adenine chloride and 3·20 and 3·38 Å in guanine hydrochloride (Broomhead, 1951); and more recently 3·165, 3·245 and 3·139 Å in cycloserine hydrochloride (Turley & Pepinsky, 1956, 1957)].

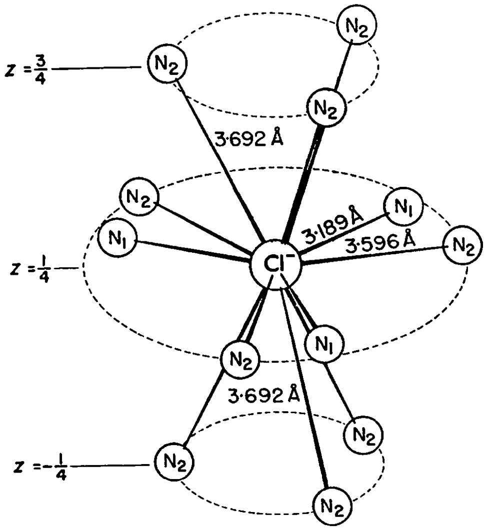

Fig. 5. Triaminoguanidinium chloride: coordination of nitrogen atoms around chlorine ion.

The triaminoguanidinium ion possesses threefold symmetry, and is planar except for the hydrogen atoms on N(II). From these results, and from the nature of the hydrogen-bond formation in this crystal, it is clear that the triaminoguanidinium ion takes a configuration as a result of the resonance among the three structures, as shown in Fig. 6, each structure having a probability one-third. The C–N distance of $1\cdot31_8$ Å is much shorter than other reported values, such as 1·33 and 1·32 Å in methylguanidinium nitrate (Curtis & Pasternack, 1955) and 1·34 and 1·35 Å in nitroguanidine (Bryden, Burkardt, Hughes & Donohue, 1956); but a direct comparison might not be worthwhile because these values pertain to monosubstituted guanidines where the resonance states are somewhat different. The N(I)–N(II) distance of $1\cdot45_0$ Å should be compared with that of hydrazine and its salts; 1·47 Å as in gaseous hydrazine (Giguère & Shomaker, 1943); 1·46 Å in solid hydrazine (Collin & Lipscomb, 1951); and 1·45 Å in hydrazinium chloride and bromide (Sakurai & Tomiie, 1952). The angle C–N(I)–N(II) is 120° within the error of experiment, and is in accord with the resonance states proposed.

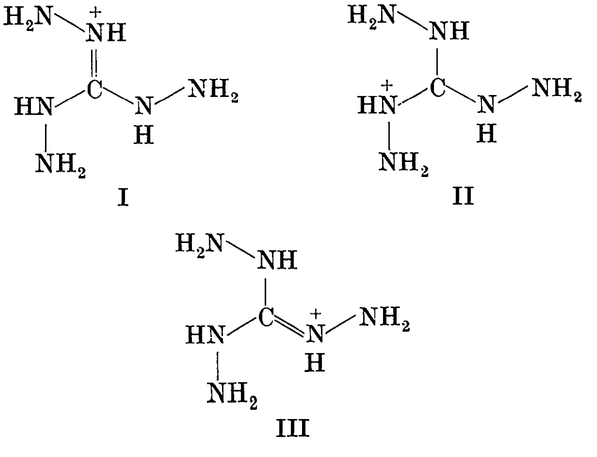

Fig. 6. Triaminoguanidinium ion: resonance formulae (one-third each).

Errors in the bond distances were assessed using the method of Cruickshank (1949). C–N(I) has a standard deviation of 0·009 Å, and N(I)–N(II) of 0·014 Å.

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