

The Crystal Structure of 1-Methylcytosine Hydrochloride*

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Crystals of 1-methylcytosine hydrochloride, $C_5H_8N_3O^+ \cdot Cl^-$, are monoclinic, space group $P2_1/n$, with $a = 6.695$ (3), $b = 32.30$ (2), $c = 6.912$ (2) Å and $\beta = 104.22$ (3)°. There are eight formula units per cell, and hence two per asymmetric unit. Data were collected on an automated diffractometer; the structural parameters were refined to an R index of 0.055 for 2609 reflections. Standard deviations in the bond distances are about 0.004 Å. Bond distances in the two structurally distinct molecules are in statistical agreement. The environments of both molecules are closely parallel; features of the structure include layers of molecules joined by $N-H \cdots O$ and $N-H \cdots Cl^-$ hydrogen bonds, relatively short $C-H \cdots O$ interactions, and close meshing of methyl groups.

Introduction

This determination of the structure of methylcytosine hydrochloride was undertaken as part of a program of research on the structures of compounds related to nucleic acids. Our particular interests in this compound were focused on the possibility of base stacking and on determining with high accuracy the geometry of a protonated form of cytosine for comparison with unprotonated forms.

Crystal data

Crystals of 1-methylcytosine hydrochloride, in the form of needles elongated along a , were prepared by the evaporation of a dilute HCl solution. These crystals were stable in air for only a few days, so the crystal from which intensity data were obtained was covered with a thin layer of epoxy resin.

The space group and approximate cell constants were obtained from Weissenberg and precession photographs; more accurate cell constants were obtained by a least-squares fit to 2θ values measured on a diffractometer. The density was measured by flotation in a chloroform-bromoform mixture. Crystal data are given in Table 1.

Table 1. *Crystal data*

$C_5H_8N_3O^+ \cdot Cl^-$	F.W. 161.6
Space group $P2_1/n$	Systematic absences:
$a = 6.695$ (3) Å	$h0l, h+l = 2n+1$;
$b = 32.30$ (2)	$0k0, k = 2n+1$
$c = 6.912$ (2)	$Z = 8$
$\beta = 104.22$ (3)°	$F_{000} = 672$
$\lambda(Cu K\alpha) = 1.5418$ Å	$D_c = 1.478$ g.cm ⁻³
$V = 1449$ Å ³	$D_m = 1.483$ g.cm ⁻³
$\mu = 41.4$ cm ⁻¹	

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Experimental

Intensity data were measured on a Datex-automated General Electric diffractometer, using Ni-filtered $Cu K\alpha$ radiation. The crystal had approximate dimensions $0.41 \times 0.32 \times 0.25$ mm, and was mounted along a , the long dimension. Reflections with $2\theta \leq 141.5^\circ$ were scanned in the $\theta-2\theta$ mode at a rate of 2° per min, the scan range varying from 2° at $2\theta = 10^\circ$ to 4° at $2\theta = 130^\circ$. A 30 sec background count was recorded on either side of the scan range. Two sets of data were measured and averaged, the crystal being rotated by 180° in ϕ between sets. Thus, a complete hemisphere of the reciprocal lattice was surveyed. The agreement in net intensity between the two data sets was very good, within the assigned standard deviations. A standard check reflection was measured every 20 reflections; the intensity of this standard decreased continuously by about 3% during the two weeks of data collection. Absorption corrections were not applied.

Altogether, 2793 independent reflections were measured. Each reflection was assigned a variance $\sigma^2(I)$ based on counting statistics plus an empirical term $(0.02s)^2$, where s is the scan count. Values of F_o^2 and $\sigma(F_o^2)$ were derived from the net intensities by application of the Lorentz and polarization factors and a time-dependent scale factor derived from the fall-off of the check reflection. Any reflection for which the net value of F_o^2 was less than or equal to zero was assigned an intensity and weight of zero. There were 2609 observations in the final data set. The 184 reflections omitted from the calculations included 11 high-angle reflections which were omitted because of grossly uneven backgrounds, apparently due to too narrow a scan range.

Structure solution and refinement

The coordinates of the chlorine atom were derived from a three-dimensional Patterson function, and a

subsequent electron density map indicated the positions of the remaining heavy atoms. The resulting structure-factor calculation gave an R value ($=\sum|F_o - F_c|/\sum|F_o|$) of 0.40. Three cycles of full-matrix least-squares adjustment of the coordinates and isotropic temperature factors lowered R to 0.17. The hydrogen atoms were then located on a difference map. Further full-matrix refinement of 246 parameters – coordinates of all 36 atoms, anisotropic temperature parameters for the 20 heavy atoms, isotropic B 's for the 16 hydrogen atoms, a secondary extinction parameter (Larson, 1967), and a scale factor – led to a final R index of 0.055, a weighted R_w [$=\sum w(|F_o|^2 - |F_c|^2)^2/\sum wF^4$, where $w=1/\sigma^2(F_o^2)$] of 0.009 and a goodness of fit ($=[\sum w(|F_o|^2 - |F_c|^2)^2/(M - S)]^{1/2}$ for $M=2609$ observations and $S=146$ parameters) of 2.4. The largest shift in the final least-squares calculation was 0.4σ .

Scattering factors were those in *International Tables for X-ray Crystallography* (1962) except for hydrogen (Stewart, Davidson & Simpson, 1965). Computations were performed at the Caltech Computing Center on IBM 7040-7094 and 360-75 systems using the CRYRM (Duchamp, 1964) and CRYM systems (D. Duchamp, J. Westphal, B. L. Trus & B. C. Wang, unpublished). Some of the crystallographic illustrations were produced by *ORTEP* (Johnson, 1965).

The final parameters of the heavy atoms appear in Table 2 and those of the hydrogen atoms in Table 3. Observed and calculated structure factors are listed in Table 4. The final value of the extinction parameter g (Larson, 1967, equation 3) was $6.8 \pm 0.4 \times 10^{-6}$.

Discussion

Molecular configuration

The bond distances and angles in the two independent methylcytosine cations are shown in Fig. 1. The standard deviations in the individual distances are

Table 3. *Coordinates and isotropic temperature parameters for the hydrogen atoms*

Standard deviations are given in parentheses

	x^*	y^\dagger	z^*	B
A				
H(1a)	512 (4)	3880 (9)	260 (5)	6.1 (0.8)
H(1b)	728 (5)	3821 (9)	222 (4)	5.8 (0.8)
H(1c)	549 (5)	3877 (10)	43 (5)	8.3 (0.9)
H(3)	475 (4)	5241 (7)	292 (4)	3.7 (0.6)
H(4a)	692 (4)	5811 (8)	330 (4)	4.5 (0.7)
H(4b)	927 (5)	5770 (9)	311 (4)	6.4 (0.8)
H(5)	1023 (4)	5042 (7)	240 (3)	3.0 (0.6)
H(6)	941 (4)	4334 (8)	175 (4)	4.1 (0.6)
H(1a)	190 (5)	3632 (9)	8 (5)	6.5 (0.8)
H(1b)	-57 (4)	3544 (8)	-12 (4)	4.8 (0.7)
H(1c)	88 (5)	3616 (9)	176 (5)	6.9 (0.8)
B				
H(3)	-73 (4)	2171 (8)	100 (4)	5.7 (0.8)
H(4a)	139 (5)	1604 (9)	96 (4)	6.5 (0.8)
H(4b)	368 (4)	1676 (8)	82 (4)	4.8 (0.7)
H(5)	494 (3)	2407 (6)	57 (3)	2.7 (0.5)
H(6)	423 (4)	3130 (8)	51 (4)	4.6 (0.6)

* $\times 10^3$. † $\times 10^4$.

about 0.004 \AA , and in the angles 0.15° . Rather surprisingly, the agreement between the dimensions of the two different molecules is considerably better than would be anticipated from the formal estimated standard deviations. Thus, whereas the standard deviation in the difference between any pair of equivalent bonds would be expected to be about 0.0056 \AA ($=0.004 \times \sqrt{2}$), the observed r.m.s. difference among the nine pairs of equivalent bonds is only 0.0025 \AA . Although this disparity is presumably only a reflection of the poor statistics of small samples, we take it as an indication that our formal e.s.d.'s are not seriously underestimated.

The average dimensions of the two cations are listed in Table 5. The standard deviations in these values – about 0.003 \AA in the distances and 0.1° in the angles – are considerably smaller than in other struc-

Table 2. *Coordinates and anisotropic temperature parameters for the heavy atoms*

Standard deviations are given in parentheses. The temperature factor has the form

$$\exp [-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)].$$

	x^*	y^{**}	z^*	b_{11}^*	b_{22}^{**}	b_{33}^*	b_{12}^{**}	b_{13}^*	b_{23}^{**}
A									
Cl(1)	2310(1)	8091(2)	1968(1)	177(2)	61(1)	264(2)	-82(5)	138(3)	61(6)
Cl(2)	7365(1)	16215(2)	908(1)	211(2)	66(1)	320(2)	-65(5)	195(3)	51(6)
N(1)	6568(3)	44117(6)	2023(3)	175(6)	66(2)	234(6)	-31(17)	181(10)	-74(18)
C(2)	5041(4)	46720(8)	2334(4)	171(7)	83(3)	214(7)	69(21)	121(11)	72(23)
N(3)	5628(3)	50814(6)	2677(4)	159(6)	71(2)	238(6)	148(17)	155(9)	25(18)
C(4)	7514(4)	52387(7)	2740(4)	169(7)	71(2)	182(7)	33(20)	111(10)	30(20)
C(5)	9007(4)	49589(8)	2395(5)	147(7)	76(3)	265(8)	-19(20)	163(12)	-59(23)
C(6)	8480(4)	45582(8)	2052(4)	182(7)	82(3)	245(8)	162(22)	167(12)	15(23)
C(1)	6079(6)	39688(9)	1754(6)	283(9)	73(3)	334(11)	-99(26)	219(17)	-99(27)
C(2)	3310(3)	45561(6)	2317(3)	163(5)	106(2)	364(7)	-51(17)	179(10)	-51(20)
N(4)	7884(4)	56338(7)	3106(4)	238(7)	65(2)	298(8)	71(20)	177(12)	-23(20)
B									
Cl(1)	1327(3)	30401(6)	663(3)	167(6)	67(2)	229(6)	43(17)	124(9)	45(18)
C(2)	-215(4)	27705(8)	844(4)	163(7)	91(3)	228(8)	16(22)	117(12)	143(23)
N(3)	329(3)	23567(6)	929(4)	159(6)	77(2)	246(7)	-86(18)	120(10)	71(19)
C(4)	2181(4)	22033(8)	853(4)	184(7)	72(2)	195(7)	-45(20)	103(11)	42(21)
C(5)	3708(4)	24920(8)	701(4)	164(7)	78(3)	259(8)	68(20)	159(12)	9(23)
C(6)	3224(4)	28991(8)	620(4)	162(7)	82(3)	239(8)	-52(21)	106(12)	25(22)
C(1)	87(5)	34857(9)	557(5)	256(9)	71(3)	312(10)	67(24)	140(15)	-14(26)
O(2)	-1932(3)	28838(6)	906(3)	163(5)	116(2)	407(8)	133(17)	227(10)	256(21)
N(4)	2483(4)	18010(7)	916(4)	255(7)	65(2)	298(8)	31(21)	175(12)	79(21)

* $\times 10^4$, ** $\times 10^5$

Table 4. Structure factors

Each group of three columns contains k, 10F₀, and 10F_c and is headed by values of h and l common to the group. Asterisks following 10F_c indicate reflections given zero weight and omitted from the refinement.

Table with multiple columns containing reflection indices (h, k, l) and structure factor values (F₀, F_c). The table is organized into groups based on h and l values, with some reflections marked with asterisks to indicate zero weight.

ture analyses of a protonated cytosine moiety, which include methylcytosine hydrobromide ($\sigma=0.04 \text{ \AA}$; Bryan & Tomita, 1962) and two forms of cytidylic acid (Sundaralingam & Jensen, 1965, $\sigma=0.006 \text{ \AA}$; Bugg & Marsh, 1967, $\sigma=0.009 \text{ \AA}$). Values from these other investigations agree with ours within their e.s.d.'s.

Also included in Table 5 are the dimensions of the neutral cytosine ring as averaged from the values of Jeffrey & Kinoshita (1963; $\sigma=0.004 \text{ \AA}$) for cytosine monohydrate and of Barker & Marsh (1964; $\sigma=0.003 \text{ \AA}$) for anhydrous cytosine crystals. Not surprisingly, the most pronounced effects of protonation of the ring are adjustments of the ring angles, focused on an enlargement of the angle at the site of protonation [N(3)] by over 6° . Significant changes in the bond distances include a lengthening of the C(2)–N(3) bond by over 0.02 \AA and shortenings of the C(4)–C(5), C(2)–O(2), and C(4)–N(4) bonds; the latter two

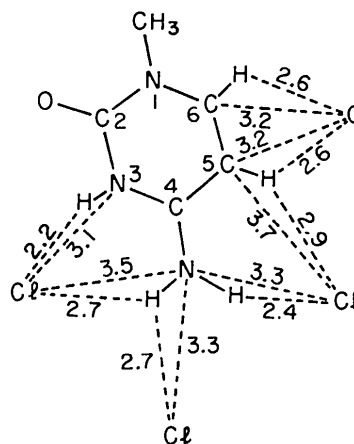


Fig. 2. Details of the hydrogen bonding scheme. The distances are averaged values for molecules *A* and *B*.

Table 5. *A comparison of the dimensions of a neutral cytosine molecule (C)* with those of the protonated species (CH⁺)†*

Standard deviations are about 0.003 \AA in the distances and 0.1° in the angles.

Bond distances	C		CH ⁺		
	C	CH ⁺	C	CH ⁺	
N(1)–C(2)	1.375 Å	1.381 Å	C(6)–N(1)–C(2)	122.0°	121.1°
C(2)–N(3)	1.359	1.383	N(1)–C(2)–N(3)	119.1	114.8
N(3)–C(4)	1.344	1.350	C(2)–N(3)–C(4)	119.4	126.1
C(4)–C(5)	1.428	1.409	N(3)–C(4)–C(5)	122.0	116.8
C(5)–C(6)	1.345	1.350	C(4)–C(5)–C(6)	117.2	118.6
C(6)–N(1)	1.359	1.359	C(5)–C(6)–N(1)	120.4	122.8
C(2)–O(2)	1.247	1.216	N(1)–C(2)–O(2)	119.1	123.4
C(4)–N(4)	1.331	1.314	N(3)–C(2)–O(2)	121.8	122.0
			N(3)–C(4)–N(4)	118.0	120.0
			C(5)–C(4)–N(4)	120.0	123.3

* Average from values for cytosine (Barker & Marsh, 1964) and cytosine monohydrate (Jeffrey & Kinoshita, 1963).

† Average of molecules *A* and *B*, this investigation.

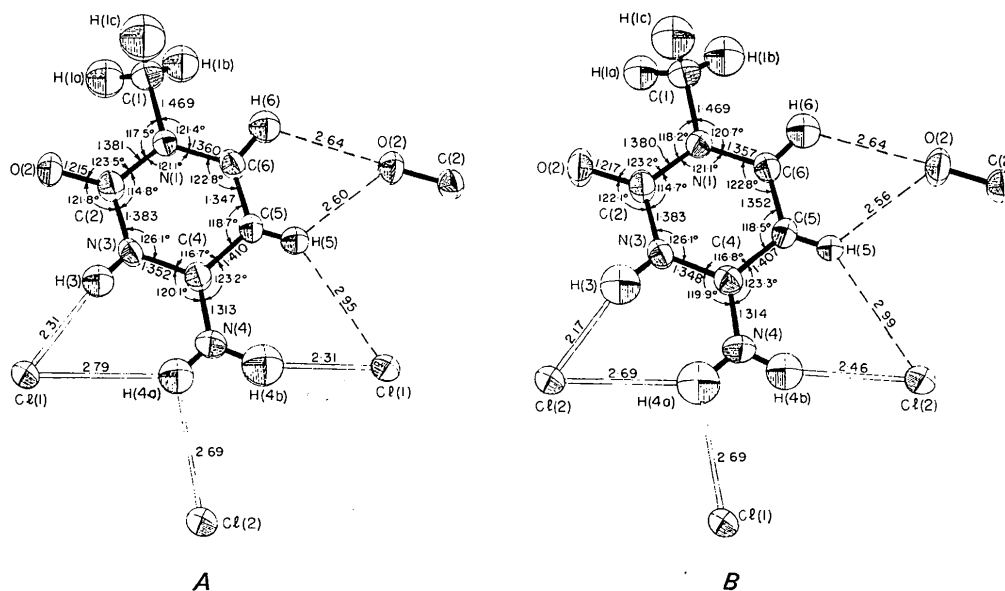


Fig. 1. Distances and angles. The standard deviations for heavy atom distances and angles are 0.004 \AA and 0.15° . Standard deviations involving hydrogen distances and angles are about ten times larger.

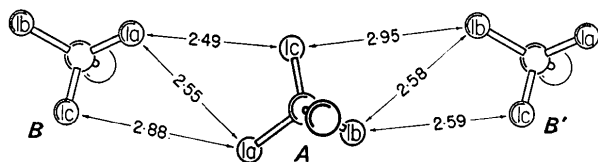


Fig. 3. Details of the packing of the methyl groups. The direction of view is approximately parallel to the b axis and to the C(1)–N(1) bonds. Methyl group B' is related to group B by a unit-cell translation in the a direction.

Table 6. *Least-squares planes of the six-membered rings*

The direction cosines (g_i) are relative to the crystal axes a , b , and c ; D is the origin-to-plane distance.

	Ring A	Ring B
g_a	–0.0492	0.0548
g_b	0.1852	0.0575
g_c	–0.9393	0.9528
D	1.112 Å	1.058 Å

	Weight	Deviation (Å)	
N(1)	7	–0.004	–0.008
C(2)	6	0.001	0.004
N(3)	7	0.003	0.003
C(4)	6	–0.005	–0.007
C(5)	6	0.002	0.002
C(6)	6	0.002	0.006
C(1)	0	–0.078	–0.012
O(2)	0	0.000	0.003
N(4)	0	–0.019	–0.030
H(1a)	0	–0.65	–0.26
H(1b)	0	–0.51	–0.51
H(1c)	0	0.75	0.81
H(3)	0	–0.03	–0.02
H(4a)	0	0.02	–0.08
H(4b)	0	–0.01	–0.07
H(5)	0	0.01	–0.06
H(6)	0	0.03	0.02

Table 7. *Bond distances and angles involving the hydrogen atoms*

The e.s.d.'s are about 0.03 Å and 2.0°.

	Molecule A	Molecule B
C(1)–H(1a)	1.01 Å	0.96 Å
C(1)–H(1b)	0.92	0.98
C(1)–H(1c)	0.95	0.93
N(3)–H(3)	0.83	0.94
N(4)–H(4a)	0.90	0.98
N(4)–H(4b)	1.03	0.91
C(5)–H(5)	0.86	0.89
C(6)–H(6)	1.01	1.02
N(1)–C(1)–H(1a)	110.9°	110.1°
N(1)–C(1)–H(1b)	108.2	112.1
N(1)–C(1)–H(1c)	116.9	116.2
C(2)–N(3)–H(3)	116.4	114.9
C(4)–N(3)–H(3)	117.5	119.0
C(4)–N(4)–H(4a)	122.7	122.4
C(4)–N(4)–H(4b)	122.9	124.3
C(4)–C(5)–H(5)	120.7	120.7
C(6)–C(5)–H(5)	120.6	120.6
C(5)–C(6)–H(6)	125.4	123.8
N(1)–C(6)–H(6)	111.8	113.4
H(1a)–C(1)–H(1b)	106.2	116.5
H(1b)–C(1)–H(1c)	107.4	97.8
H(1a)–C(1)–H(1c)	107.3	103.7
H(4a)–N(4)–H(4b)	114.3	113.2

changes, which involve exocyclic atoms, may reflect in part changes in the hydrogen bonding. The expected lengthening of the N(3)–C(4) bond, by 0.006 Å, is too small to be of statistical significance.

Both six-membered rings are closely planar (see Table 6), but some of the exocyclic atoms are significantly out-of-plane. Bond distances and angles involving hydrogen atoms are given in Table 7.

Packing

The hydrogen bonding arrangement is essentially identical for both methylcytosine cations (see Fig. 1).

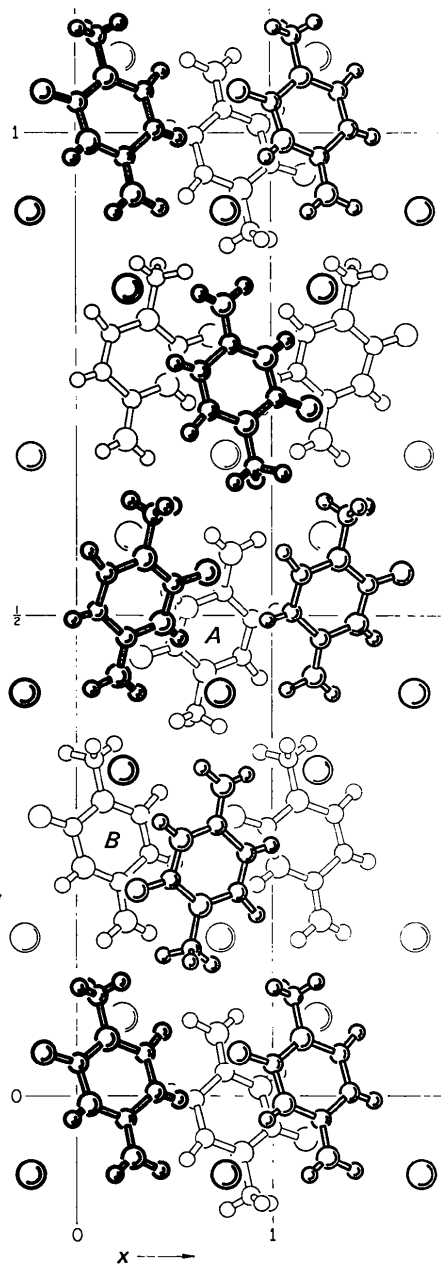


Fig. 4. View down the c axis.

Further details, including average distances, are shown in Fig. 2. Of special note is the nicely bifurcated arrangement about one of the -NH_2 protons and the relatively short $\text{C-H}\cdots\text{O}$ contacts which, depending on one's personal prejudices, may or may not be hydrogen bonds. [True aficionados of hydrogen bonds involving C-H groups may wish to add to their lists the $\text{C(5)-H(5)}\cdots\text{Cl}$ groupings.] The hydrogen bond system shown in Fig. 2, including the $\text{C-H}\cdots\text{O}$ arrangement, is very similar to that found in crystals of methylcytosine hydrobromide (Bryan & Tomita,

1962); in the latter compound, bromide ions replace chloride in the positions at the two sides of the -NH_2 group, but a methyl group (at a rather short distance $\text{N}\cdots\text{C}$ of 3.2 \AA) replaces the chloride ion in the head-on position.

A second facet of the intermolecular arrangement is a tight interlocking of methyl groups along the \mathbf{a} direction. Details of the packing are shown in Fig. 3. As a result of the relatively short $\text{H}\cdots\text{H}$ contacts, the hydrogen atoms are entirely ordered and their temperature factors (Table 3) are smaller than usually found for methyl groups. This packing may also be responsible for the displacement of the methyl group of cation A from the best plane of the pyrimidine ring (Table 6). For both cations the conformation about the N(1)-C(1) bond is *gauche*, whereas in methylcytosine hydrobromide (Bryan & Tomita, 1962) one methyl hydrogen atom is required by symmetry to be eclipsed with respect to the benzene ring.

Packing drawings of the structure are shown in Figs. 4 and 5. Methylcytosine cations of type A lie near $y=0$ and $\frac{1}{2}$, while those of type B lie near $y=\frac{1}{4}$ and $\frac{3}{4}$. Hydrogen bonds involving the chloride ions connect an A cation with a B , forming ribbons two molecules wide, stretching along the \mathbf{a} direction and oriented parallel to the ab plane. Adjacent ribbons in the same plane are held together by interactions between methyl groups (see Fig. 3). The packing forces between planes appear to be predominantly electrostatic, involving the

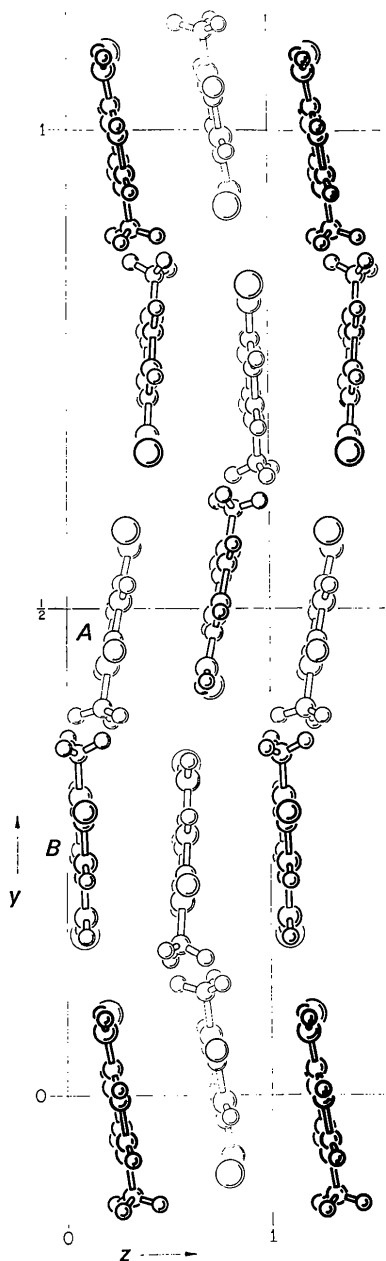


Fig. 5. View up the \mathbf{a} axis.

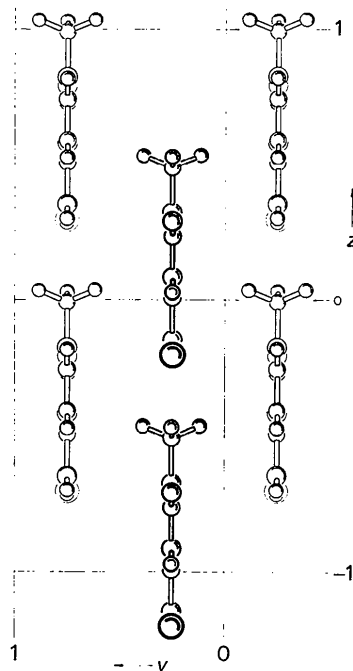


Fig. 6. The structure of methylcytosine hydrobromide (Bryan & Tomita, 1962) as viewed down the \mathbf{a} axis.

chloride ions. There is little stacking overlap between adjacent cytosine rings; rather, each ring lies above (and below) the gap between two rings in the neighboring planes. By comparison, in the hydrobromide salt (Bryan & Tomita, 1962) each methylcytosine cation lies above the gap in the center of four rings in the neighboring sheet (Fig. 6).

The close similarity in the intermolecular environments of the two molecules in the asymmetric unit is reflected in their similar patterns of thermal motion (Fig. 1).

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Monoclinic Structure of Synthetic $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$, Chlorapatite

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Apatites are normally expected to be hexagonal, with space group $P6_3/m$ ($Z=2$), but nearly stoichiometric synthetic chlorapatite is pseudohexagonal, with monoclinic space group $P2_1/b$ ($Z=4$, $a=9.628$ (5) Å, $b=2a$, $c=6.764$ (5) Å, $\gamma=120^\circ$). The monoclinic and hexagonal structures are very similar, the most significant feature of the monoclinic structure being an ordered arrangement of the Cl atoms above and below $z=\frac{1}{2}$ on the pseudohexagonal axis, such that the mirror plane of the hexagonal structure becomes a glide plane in the monoclinic structure with the doubling of one cell dimension. The mechanism by which the needed ordering information propagates from one Cl column to another involves the occurrence of a Cl atom near the center of one of the two axial triangles of oxygen atoms. The presence of the Cl atom expands the oxygen triangle, thus tilting the associated phosphate tetrahedra and setting off a distortion, propagating *via* ~ 0.05 Å displacements of columnar Ca ions, which affects the selection of Cl positions in the adjacent unit cells. An active role of Cl vacancies in promoting occurrence of the hexagonal phase, and in the apparent development of ferroelectric character in an applied electric field, is suggested. X-ray intensity data from two single-crystal specimens were collected with an automatic diffractometer and led to $R_2(|F|^2) \geq 3.4\%$ in least-squares refinements of the structure.

Introduction

By analogy with other apatites that have the space group $P6_3/m$, it has been generally presumed that chlorapatite is hexagonal, with the chlorine ion in the special position at $z=\frac{1}{2}$ (Hendricks, Jefferson & Mosley, 1932). However, nearly stoichiometric synthetic chlorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$, exhibits the monoclinic space group $P2_1/b$ (Young & Elliot, 1966). A mineral chlorapatite of nearly stoichiometric chlorine content has also been reported to be similarly monoclinic (Hounslow & Chao, 1970), as have both mineral and synthetic mimetite, $\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$ (Keppler, 1968, 1969). Because monoclinic chlorapatite exhibits al-

most complete structural similarity to the hexagonal ($P6_3/m$) apatites fluorapatite and hydroxyapatite, the monoclinic cell setting that has the c axis as the unique axis has been chosen to accommodate this similarity. The difference lies primarily in the placement of the halogen ions on columns about 9.6 Å apart. A particular point of interest in the present work is the mechanism by which the ordering information is propagated from column to column, changing the mirror plane of the structure with space group $P6_3/m$ into the glide plane of the structure with space group $P2_1/b$.

The apatite structure has been pictured many times in the literature, most notably by the color overlays in the paper by Beevers & McIntyre (1946). Fig. 1 illustrates the relationship between the unit cell with hexagonal symmetry, generally used for apatites, and the monoclinic unit cell used here. The content of an

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