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The Crystal Structure and Phase Transition of Ammonium Hydrogen Di-Chloroacetate. I. The Crystal Structure of the Paraelectric Phase

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The crystal structure of ferroelectric ammonium hydrogen di-chloroacetate, $NH_4H(ClCH_2COO)_2$, has been determined by three-dimensional X-ray analysis at room temperature (paraelectric phase). The crystals are monoclinic, with the space group $C2/c$, and cell dimensions $a=10\cdot521$, $b=11\cdot576$, $c=8\cdot387$ Å, $\beta=119\cdot48°$; $Z=4$. The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares method using data collected on both Weissenberg photographs and an automatic diffractometer. The final R is 0·068. Each ammonium ion lies on a twofold axis and makes a hydrogen bond with an oxygen atom from each of six different chloroacetate residues. The acidic hydrogen atom is involved in a very short hydrogen bond, $O\cdots O=2\cdot432\pm0\cdot005$ Å, which connects two chloroacetate residues across a centre of symmetry. The significance of such a crystallographically symmetrical hydrogen bond is discussed.

Introduction

Ammonium hydrogen di-chloroacetate, $NH_4H(ClCH_2COO)_2$, is ferroelectric below 128°K (Ichikawa & Mitsui, 1966). To elucidate the nature of mechanism of the ferroelectric phase transition, the ^{35}Cl nuclear quadrupole resonance (NQR) frequencies were measured in a polycrystalline sample (Yamamoto, Nakamura & Chihara, 1968, 1970). The present paper deals with a three-dimensional X-ray diffraction study, which has been carried out at room temperature (paraelectric phase) in order to clarify the structural change accompanying the ferroelectric phase transition and to examine the hydrogen bonding. This is the first part of the structural studies on this compound.

Experimental

The crystal data of ammonium hydrogen di-chloroacetate are given in Table 1, of which preliminary results were previously reported (Ichikawa & Mitsui, 1966). Unit-cell parameters at room temperature were obtained from a least-squares treatment, using values of θ for 74 reflexions measured on zero-layer Weissenberg photographs taken around each crystallographic axis with Cu $K\alpha$ radiation.

Table 1. *Crystal data*

$a=10\cdot521$ (4) Å
$b=11\cdot576$ (4)
$c=8\cdot387$ (3)
$\beta=119\cdot48$ (3)°
$V=889\cdot2$ (5) Å^3

Formula: $NH_4H(ClCH_2COO)_2$
Space group $C2/c$
F.W. 206·0
$\varrho_m=1\cdot528$ g.cm^{-3}
$\varrho_c=1\cdot538$ g.cm^{-3}
$F(000)=424$
$Z=4$
$\lambda(\text{Cu }K\alpha_1)=1\cdot5405$ Å

Two sets of three-dimensional intensity data were used in this work. A set of data obtained by photographic methods were replaced by data collected on a diffractometer at the stage of the refinement of structure. The first set was obtained from integrated equi-inclination Weissenberg photographs taken with Cu $K\alpha$ radiation using the multiple film technique about a, b and c axes (layer: $h=0\sim6$; $k=0\sim7$; and $l=0\sim5$). Cylindrical crystals with dimensions of $0\cdot22\sim0\cdot24$ mm in diameter were used. The intensities were measured by visual comparison with a calibrated scale. They were corrected for Lorentz and polarization factors, absorption corrections being applied (μCu $K\alpha=63$ cm^{-1}). Absorption correction factors used for calculation were taken from *International Tables for X-ray Crystallography* (1959). Corrections for the elongation of spots on the high layers were made according to Phillips (1956). The data from each layer were correlated by the method of Rollett & Sparks (1960) and then placed on an absolute scale by Wilson's (1949) method. A total of 738 independent reflexions were obtained, of which 227 were too weak to be measured.

The second set of data was obtained on a Rigaku Denki automatic four-circle diffractometer, AFC, controlled by a FACOM 270-20 computer. A spherical crystal with dimension of 0·35 mm in diameter was used. Integrated intensities were collected for $2\theta\le70°$ by the ω–2θ scanning technique with Mo $K\alpha$ radiation monochromated with a LiF crystal. A scanning speed of 2° per min was employed and the scanning range varied by $\Delta 2\theta=2°+0\cdot8°\tan\theta$. Background was measured for twenty seconds at the beginning and at the end of each scan. As a check on the stability of the crystal and the instruments, three standard reflexions were measured every fifty reflexions: no significant variation in their intensities was noted. No correction was made for absorption (μMo $K\alpha=7\cdot0$ cm^{-1}). 1967 reflexions were measured, of which 706 had $|F_o|$

values less than three times the relevant standard deviation derived from counting statistics, and were given the value zero. The calculation of the unit-cell parameters and the whole processing of intensity data were carried out on a HITAC 5020E computer with *UNICS* (1967).

Determination and refinement of the structure

The structure determination was initiated using the photographic data. The coordinates of the chlorine atoms were determined from a three-dimensional sharpened Patterson function. Four cycles of Fourier iterations led to an R value $(\sum|k|F_o|-|F_c||/\sum k|F_o|)$ of 0·26. Refinement was carried out using a block-diagonal least-squares method for positional parameters, and individual isotropic and anisotropic temperature factors. The R value was reduced to 0·09. The quantity minimized was $\sum w(|F_o|-1/k|F_c|)^2$. A difference Fourier synthesis revealed all the hydrogen atoms at the expected positions.

At this stage the diffractometer data became available and subsequent least-squares calculations were performed with these data. The starting parameters were those obtained in the final cycle of the isotropic refinement using photographic data. Refinement was carried out on the coordinates of heavy atoms with anisotropic temperature factors and on the coordinates of hydrogen atoms with isotropic temperature factors. The temperature factor of the H(3) atom, however, was given a fixed value of the overall temperature factor, because its value was found to be unusually large. All parameter shifts were less than one tenth of their standard deviations in the final cycle. The standard deviations of the parameters were calculated from the sum of the weighted residuals and the diagonal terms of the inverse matrix of the normal equations. Unit weight was assigned for all the reflexions, except those with zero intensity and five strong reflexions which are likely to be affected by extinction; these five reflexions were given zero weight in the refinement. The damping factor of 0·8 was applied to the scale factor, the overall temperature factor and also to the parameters of the heavy atoms, and 0·1 to those of the hydrogen atoms. The final R value was 0·068. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

Fourier, least-squares, bond-length and bond-angle, and best-plane calculations were done on a HITAC 5020E and a FACOM 230-60 computer with *UNICS* (1967). The final positional parameters and temperature factors are given in Tables 2 and 3, together with their standard deviations; a list of $|F_o|$ and F_c values for the counter data is given in Table 4. In Fig. 1 a composite drawing of a three-dimensional electron-density map is shown, while in Fig. 2 that of a difference map is shown, for which the contributions of the hydrogen atoms were excluded from the calculated structure factors.

Table 2. *The atomic positional parameters and their standard deviations* ($\times 10^4$)

	x	y	z
Cl	1842 (1)	4237 (1)	−607 (1)
O(1)	1770 (2)	2548 (2)	3340 (3)
O(2)	3401 (2)	3781 (2)	3363 (3)
N	0	453 (3)	2500
C(1)	1161 (3)	3404 (3)	575 (4)
C(2)	2242 (3)	3255 (2)	2580 (4)
H(1)	2500	2500	5000
H(2)	727 (37)	−45 (31)	2366 (47)
H(3)	351 (40)	820 (30)	3521 (43)
H(4)	906 (37)	2678 (31)	−55 (45)
H(5)	283 (43)	3785 (32)	479 (50)

Table 3. *The temperature factors and their standard deviations* ($\times 10^4$)

The anisotropic temperature factors are of the form:

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

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl	144 (1)	127 (1)	207 (2)	−69 (2)	76 (2)	98 (2)
O(1)	140 (3)	96 (2)	243 (5)	−107 (4)	182 (6)	8 (5)
O(2)	92 (2)	69 (2)	193 (4)	−48 (3)	121 (5)	−4 (4)
N	80 (3)	55 (2)	291 (9)	0	126 (9)	0
C(1)	106 (3)	92 (3)	232 (7)	−61 (5)	84 (8)	30 (7)
C(2)	89 (3)	54 (2)	208 (5)	−21 (4)	133 (7)	−16 (5)
H(1)	8·1 (1·9)					
H(2)	3·7 (0·8)					
H(3)	4·1 (−)					
H(4)	3·6 (0·8)					
H(5)	4·7 (0·9)					

Result and discussion

The structure viewed along the a and b axes is shown in Figs. 3 and 4, respectively. A layer of ammonium ions, lying in the $(40\bar{4})$-planes, has a layer of chloroacetate residues on either side, and *vice versa*, and the packing between the ammonium ion and the chloroacetate residue is dominated by a three-dimensional network of hydrogen bonds. Moreover, two chloroacetate residues are related to one another by a symmetry centre, across which they are linked by a hydrogen bond involving the acidic hydrogen atom. According to Shrivastava & Speakman (1961), these structural features of ammonium hydrogen di-chloroacetate are

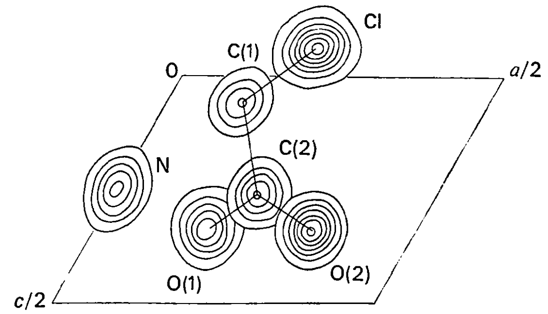

Fig. 1. A composite drawing of the final electron-density map, viewed along b axis. Contours are drawn at intervals of 4 e.Å^{-3} for the chlorine atom and 2 e.Å^{-3} for the other atoms, beginning with 2 e.Å^{-3}.

Table 4. *Observed and calculated structure factors* (× 10)

K	FO	FC
H,L= 0 0		
2	75	-59
4	462	-464
6	506	-500
8	64	-53
10	145	-141
12	113	107
14	40	-44
16	35	31
18	24	14
H,L= 1 0		
1	145	-127
3	285	307
5	52	-34
7	158	153
9	94	93
11	73	-73
13	97	-97
15	22	11
H,L= 2 0		
2	320	320
4	227	229
6	331	325
8	39	33
10	40	-40
12	133	-133
14	22	26
16	35	-26
H,L= 3 0		
1	756	799
3	211	194
5	40	28
7	454	-452
9	272	-278
11	65	65
13	89	98
15	33	-32
H,L= 4 0		
2	131	131
4	162	155
6	18	20
8	149	-143
10	44	46
12	23	17
14	46	-49
16	30	-6
H,L= 5 0		
1	233	-233
3	20	-31
5	170	174
7	220	208
9	44	45
11	124	-123
13	50	-54
15	23	-9
H,L= 6 0		
0	681	669
2	181	181
4	43	-36
6	359	-367
8	23	21
10	57	-58
12	30	-26
16	32	24
H,L= 7 0		
1	203	219
3	105	-99
5	130	-133
7	39	43
9	30	-21
11	29	24
13	32	-37
H,L= 8 0		
0	202	-203
2	72	-70
6	270	275
8	29	-20
10	29	-31
12	55	-49
14	30	-9
H,L= 9 0		
1	23	13
3	204	206
7	161	-155
9	24	-19
11	51	-49
H,L= 10 0		
0	67	81
2	43	43
6	49	-49
8	43	-38
10	31	-17
12	43	37
H,L= 11 0		
1	36	-33
3	36	-38
5	81	78
7	35	36
9	31	-15
H,L= 12 0		
0	52	50
2	37	38
6	54	-51
12	43	-30
H,L= 13 0		
1	61	59
5	55	-51
7	28	8
H,L= 14 0		
6	39	31
H,L= -15 1		
3	58	-45
H,L= -13 1		
3	33	18
5	28	-6
7	31	-23
9	25	24
H,L= -12 1		
2	51	-55
4	50	-51
6	37	-51
8	37	-28
10	56	62
H,L= -11 1		
1	95	93
3	67	76
5	102	-104
7	25	-5
9	66	-63
13	37	27
H,L= -10 1		
4	95	95
8	26	-15
10	59	-58
H,L= -9 1		
1	170	-172
3	337	-340
5	36	34
7	33	-35
9	61	66
11	31	0
H,L= -8 1		
4	109	-115
8	52	-48
10	49	-47
12	45	-9
14	53	52
H,L= -7 1		
1	74	57
3	270	264
5	23	14
7	23	24
9	123	-126
11	34	-39
H,L= -6 1		
2	118	-125
4	379	-370
6	228	-228
8	97	88
10	174	167
H,L= -5 1		
1	149	-138
3	139	130
5	260	-253
7	277	-276
11	120	130
13	29	-27
15	27	25
H,L= -4 1		
2	357	360
4	397	374
6	69	71
8	137	-140
10	248	-251
12	39	35
14	22	15
H,L= -3 1		
1	232	227
5	94	-96
7	133	126
9	166	154
11	108	-120
13	87	86
H,L= -2 1		
4	163	-150
8	153	-134
10	96	97
14	31	23
16	39	41
H,L= -1 1		
1	36	38
5	28	-22
9	309	-305
11	67	-67
15	58	57
H,L= 0 1		
2	435	425
4	757	-782
6	310	-302
8	102	90
10	64	70
12	45	43
16	28	-31
18	30	33
H,L= 1 1		
1	405	-406
3	548	-560
5	416	-406
7	274	-267
9	168	169
11	167	172
15	29	-29
H,L= 2 1		
2	643	647
4	507	499
6	115	-114
8	161	-161
10	108	-107
12	67	-75
16	55	56
H,L= 3 1		
1	81	-73
3	577	-558
5	146	148
7	35	-40
9	41	-42
11	55	-63
13	65	64
H,L= 4 1		
2	652	-655
4	544	-545
6	25	21
8	149	153
12	59	54
14	24	24
H,L= 5 1		
1	97	-96
3	420	403
5	32	22
7	33	29
9	173	-175
11	24	-30
13	29	-22
15	45	45
H,L= 6 1		
2	57	54
4	112	122
6	109	-114
8	196	-201
10	75	78
H,L= 7 1		
1	101	102
3	245	-241
5	301	-291
7	21	-14
9	129	131
11	29	21
13	34	28
H,L= 8 1		
2	103	98
4	50	39
8	23	-10
10	44	-48
H,L= 9 1		
1	41	-41
3	26	15
5	81	84
7	90	-94
9	29	-30
15	31	31
H,L= 10 1		
2	122	-123
4	131	-131
6	31	-21
8	57	53
H,L= 11 1		
1	26	-29
7	37	39
9	62	-51
H,L= 12 1		
2	34	46
4	33	23
6	24	-22
8	47	-46
H,L= 13 1		
5	30	-28
7	31	-37
H,L= -14 2		
0	35	-32
6	29	-35
8	52	52
H,L= -13 2		
1	49	48
3	53	-49
7	41	-39
11	37	31
H,L= -12 2		
0	117	-118
6	65	64
8	34	-35
H,L= -11 2		
1	175	-176
3	69	63
7	31	31
9	32	33
11	29	30
H,L= -10 2		
0	183	181
2	30	-29
4	43	-37
6	86	-85
8	26	-10
12	49	59
14	29	27
H,L= -9 2		
3	77	-75
5	45	42
7	64	49
H,L= -8 2		
0	117	-122
2	191	-190
4	106	-114
6	137	129
8	196	199
10	44	47
14	33	-32
H,L= -7 2		
1	199	197
5	261	-259
7	152	-145
9	129	128
13	74	66
H,L= -6 2		
0	448	-454
2	211	197
4	75	69
6	99	92
8	210	-218
10	71	65
16	32	2
H,L= -5 2		
1	740	-729
3	204	-204
5	503	495
7	332	319
9	109	-107
11	94	94
15	37	-40
H,L= -4 2		
0	196	206
2	131	-102
4	226	220
6	542	-526
8	105	114
10	32	27
12	98	88
14	54	51
H,L= -3 2		
1	255	227
3	36	30
5	268	-265
7	91	-96
9	61	48
11	28	-26
13	27	24
15	42	48
H,L= -2 2		
0	371	-369
2	767	-778
4	540	-526
6	750	735
8	279	287
12	63	-60
14	52	-59
18	29	19
H,L= -1 2		
1	53	56
3	116	-118
5	324	-307
7	149	-134
9	167	171
11	67	62
H,L= 0 2		
0	53	47
2	453	431
4	217	-225
6	254	-251
8	179	-187
10	22	19
12	48	56
14	86	93
16	32	-19
18	34	-13
H,L= 1 2		
3	94	81
5	530	524
7	229	222
11	23	19
15	26	-18
H,L= 2 2		
0	84	84
2	524	-512
4	344	325
6	118	-113
8	19	-4
12	119	115
14	32	-35
H,L= 3 2		
1	524	515
3	111	-114
5	378	-366
7	132	-129
9	44	-36
11	74	73
13	49	49
15	29	24
H,L= 4 2		
0	635	-623
2	31	-15
4	147	-135
6	136	125
8	229	229
10	98	105
12	120	-120
H,L= 5 2		
3	234	-229
5	65	65
7	125	127
9	38	34
11	24	-21
H,L= 6 2		
0	310	309
2	91	92
4	109	-114
6	92	-91
8	129	-131
12	78	82
H,L= 7 2		
1	278	-267
3	105	109
5	56	56
9	78	73
H,L= 8 2		
0	116	-126
2	118	-123
4	90	94
6	60	63
8	40	36
10	32	-34
12	33	29
H,L= 9 2		
1	100	103
5	60	-66
7	68	-63
11	60	63
H,L= 10 2		
0	33	-24
4	63	-69
6	23	12
8	38	36
10	44	43
H,L= 11 2		
1	42	-44
3	29	-27
7	48	43
9	36	32
11	35	-26
H,L= 12 2		
8	25	-5
H,L= -14 3		
2	27	37
4	76	71
H,L= -13 3		
1	66	67
7	40	27
9	38	37
H,L= -12 3		
2	50	-41
6	23	22
H,L= -11 3		
1	28	-30
3	92	88
5	116	117
7	24	19
9	52	-53
11	41	-43
H,L= -10 3		
2	68	-67
6	114	117
8	61	64
12	51	-58
H,L= -9 3		
1	28	-37
3	64	-59
5	157	-163
7	96	93
9	28	21
11	73	74
15	29	-23
H,L= -8 3		
2	409	406
4	214	207
6	132	-123
10	60	-49
14	29	-13
H,L= -7 3		
1	126	119
3	78	78
5	338	337
7	151	-151
9	130	126
13	67	-66
15	45	-36
H,L= -6 3		
2	236	-223
4	342	-335
6	77	75
8	99	96
10	77	85
12	52	54
14	25	3
16	45	-51
H,L= -5 3		
1	36	34
3	378	363
7	202	208
9	204	-196
11	96	-88
13	49	57
15	32	29
H,L= -4 3		
2	264	-250
4	549	532
6	381	380
8	60	-56
10	33	-48
12	79	-89
H,L= -3 3		
1	268	-266
3	460	-454
5	305	-294
7	163	152
9	232	230
11	86	89
13	42	-41
15	24	-12
H,L= -2 3		
2	741	730
4	218	206
6	198	-189
8	24	-16
10	44	-26
12	54	63
H,L= -1 3		
1	886	877
3	477	472
5	475	467
7	167	-163
11	66	-72
15	52	-46
17	25	12
H,L= 0 3		
2	444	-449
4	329	-325
6	77	-72
8	207	202
10	203	192
14	31	-32
18	28	-23
H,L= 1 3		
1	602	-578
3	100	90
5	82	84
7	160	161
9	121	-111
11	34	34
15	30	15
H,L= 2 3		
2	465	448
4	249	238
6	329	323
8	32	-15
10	208	-215
12	43	-43
14	45	48
H,L= 3 3		
1	183	-185
3	307	-309
5	49	-36
7	57	64
9	118	114
11	38	42
15	26	-22
H,L= 4 3		
2	92	-96
4	88	85
6	80	-80
10	113	126
14	38	-45
H,L= 5 3		
1	418	419
3	343	340
5	82	80
11	72	-67
H,L= 6 3		
2	52	-56
4	74	-71
8	47	50
10	26	23
12	31	29
14	35	-24
H,L= 7 3		
1	161	-168
3	67	-73
5	26	-24
7	58	67
9	35	37
11	26	24
13	36	-35
H,L= 8 3		
2	82	83
4	116	113
6	93	91
8	28	-23
10	49	-47
12	36	-32
H,L= 9 3		
3	32	-30
5	28	29
H,L= 10 3		
2	24	-7
4	42	-43
8	40	35
H,L= 11 3		
1	27	19
3	53	59
5	42	42
7	30	-22
H,L= 12 3		
2	27	19
H,L= -16 4		
2	37	35
H,L= -15 4		
5	27	15
H,L= -14 4		
0	26	24
H,L= -13 4		
3	63	73
7	34	-47
9	35	-46
H,L= -12 4		
0	43	-46
4	43	47
6	46	41
8	39	44
10	52	-53
12	30	-29
H,L= -11 4		
1	81	85
3	75	-78
7	22	-13
9	43	47
13	23	-13
H,L= -10 4		
0	228	248
2	131	147
4	153	-156
8	77	-91
14	26	15
H,L= -9 4		
1	113	-116
3	151	156
7	74	84
11	64	-71
13	62	-63
H,L= -8 4		
2	115	-123
4	147	160
6	84	-80
10	28	28
12	43	42
14	35	-49
H,L= -7 4		
1	270	289
7	180	-201
9	197	-214
11	42	56
13	64	72
H,L= -6 4		
0	406	-424
2	77	76
4	239	233
6	79	79
10	83	-88
12	87	-90
H,L= -5 4		
1	52	-56
3	126	-136
7	108	130
9	137	155
11	66	-79
H,L= -4 4		
0	811	869
2	460	484
4	541	-551
6	138	-146
8	151	-162
10	29	37
12	22	-5
H,L= -3 4		
1	38	25
3	102	90
5	95	98
7	73	56
9	73	-86
11	46	-43
13	77	-80
H,L= -2 4		
0	198	-217
2	433	-446
4	373	361
6	70	80
8	199	219
10	69	-79
16	31	-25
H,L= -1 4		
1	249	259
3	401	433
5	184	-177
7	330	-353
9	74	-82
11	51	53
13	52	54
17	32	-23
H,L= 0 4		
0	81	50
2	122	121
4	82	88
6	175	175
8	198	-219
10	55	-59
12	21	18
14	29	-19
H,L= 1 4		
1	223	-239
3	135	-141
5	208	225
7	219	241
9	57	63
11	63	-69
13	44	-54
15	33	-23
H,L= 2 4		
0	275	286
2	354	372
4	166	-178
6	280	-295
10	52	51
12	53	-61
14	35	25
H,L= 3 4		
1	287	296
3	79	-90
5	66	-66
9	56	-66
11	36	-26
H,L= 4 4		
0	175	-185
2	242	-256
4	176	193
6	156	171
8	63	68
10	33	-45
14	41	-44
H,L= 5 4		
1	40	31
3	137	142
5	44	-42
7	90	-94
9	33	-39
H,L= 6 4		
0	67	71
2	126	131
4	32	-30
6	46	-48
8	81	-87
10	23	-8
H,L= 7 4		
1	104	-109
5	78	86
7	28	43
9	30	22
11	23	-12
13	34	-25
H,L= 8 4		
0	96	100
2	26	11
4	38	-38
H,L= 9 4		
1	77	83
3	21	13
5	56	-61
7	37	-30
H,L= 10 4		
0	46	-47
4	29	27
H,L= 11 4		
5	30	29
H,L= -16 5		
6	30	-25
H,L= -15 5		
5	27	-24
7	26	-27
H,L= -14 5		
6	33	36
10	36	-27
H,L= -13 5		
1	78	-81
3	60	-59
5	37	-31
7	31	35
H,L= -12 5		
2	71	-74
6	45	-53
8	38	-24
H,L= -11 5		
1	133	134
5	23	30
9	26	-17
11	57	-59
H,L= -10 5		
2	26	30
4	136	-139
6	69	-65
8	57	55
10	77	73
H,L= -9 5		
1	114	-117
3	53	41
5	63	-71
7	176	-177
9	30	-9
11	88	98
H,L= -8 5		
2	155	148
4	87	93
6	51	60
8	89	-86
10	99	-102
16	28	4
H,L= -7 5		
1	186	-189
3	227	-214
5	90	-86
7	212	209
9	22	-10
13	23	-1
H,L= -6 5		
2	379	-361
4	112	-131
6	82	-92
12	56	67
16	26	19
H,L= -5 5		
1	345	331
3	160	155
5	204	212
7	216	-209
9	48	-33
11	106	-109
15	35	38
H,L= -4 5		
2	40	46
4	105	-104
6	27	-32
8	44	30
10	77	73
14	38	-42
H,L= -3 5		
1	66	-55
3	119	-110
5	478	-491
9	38	42
11	98	114
13	30	38
H,L= -2 5		
2	259	265
4	296	301
6	57	-54
8	200	-189
10	57	-58
12	37	-34
14	25	30
16	39	35
H,L= -1 5		
1	270	-265
3	125	-126
5	190	197
7	62	58
9	29	-42
13	33	-26
H,L= 0 5		
2	318	-306
4	463	-466
6	25	-33
8	161	162
10	29	-22
12	45	49
14	35	35
H,L= 1 5		
1	163	167
3	90	89
5	169	174
7	141	-144
9	95	-89
11	47	-36
13	31	29
H,L= 2 5		
2	103	98
4	162	163
6	49	-48
8	62	-65
10	32	26
12	25	-24
14	36	-20
H,L= 3 5		
1	103	-98
3	133	-131
5	299	-307
7	41	36
9	78	81
11	57	64
15	25	-6
H,L= 4 5		
2	78	87
8	65	-63
10	24	-23
H,L= 5 5		
1	43	44
3	55	61
5	68	71
11	43	-44
15	25	17
H,L= 6 5		
2	197	-194
4	93	-97
8	36	24
H,L= 7 5		
3	30	-21
H,L= 8 5		
2	94	96
4	29	28
H,L= 9 5		
1	46	-46
3	34	-24
9	26	12
H,L= -16 6		
6	26	8
H,L= -15 6		
1	36	-37
H,L= -14 6		
0	24	-34
8	28	-1
H,L= -13 6		
3	27	-24
5	23	2
H,L= -12 6		
0	54	49
2	88	-92
4	46	-45
6	43	46
8	69	73
H,L= -11 6		
3	35	38
5	110	-106
7	56	-53
9	66	67
H,L= -10 6		
0	70	-52
4	79	84
8	57	-60
10	27	-28
H,L= -9 6		
1	156	-168
3	66	-72
5	187	180
7	65	67
11	23	2
15	31	-33
H,L= -8 6		
0	76	-86
2	82	78
4	107	-105
6	45	-29
8	48	-45
10	92	97
12	29	24
14	31	29
H,L= -7 6		
1	110	121
3	34	37
5	122	-125
9	41	-48
11	29	-28
15	49	48
H,L= -6 6		
0	30	-31
2	235	-240
4	60	48
6	84	80
8	203	213
12	50	-54
14	39	-38
H,L= -5 6		
1	95	91
3	185	-187
5	85	-70
9	57	69
11	103	103
15	29	-26
H,L= -4 6		
0	86	90
2	174	187
4	28	-19
6	124	-124
8	117	-130
10	25	-26
12	34	48
14	56	52
H,L= -3 6		
1	450	-451
3	194	182
5	235	223
7	45	43
9	30	47
11	56	-55
H,L= -2 6		
0	104	-94
2	90	-85
4	118	-123
6	128	138
8	48	-31
10	66	71
12	73	61
H,L= -1 6		
1	286	287
3	33	-21
5	191	-187
7	122	-123
9	48	-47
11	42	44
13	35	27
H,L= 0 6		
0	115	-119
2	148	-158
4	106	106
6	52	-8
8	166	173
10	30	-27
12	69	-66
16	30	19
H,L= 1 6		
1	79	-66
3	134	-145
7	121	132
9	51	57
13	23	-5
H,L= 2 6		
0	155	159
2	125	132
4	75	-77
6	105	-105
8	120	-124
10	30	33
12	43	45
14	24	13
H,L= 3 6		
1	113	-126
3	24	24
5	100	101
9	26	-20
H,L= 4 6		
0	209	-208
2	60	-62
4	42	44
6	53	56
8	38	45
H,L= 5 6		
1	90	102
5	77	-79
7	70	-69
11	30	26
H,L= 6 6		
0	83	76
2	48	-45
4	32	-27
6	30	22
H,L= 7 6		
1	67	-72
5	22	11
7	48	44
9	36	32
H,L= 8 6		
2	45	33
6	28	-24
H,L= 9 6		
5	24	14
H,L= -15 7		
5	37	34
H,L= -14 7		
2	37	-40
6	50	37
10	30	14
H,L= -13 7		
1	28	25
5	50	-47
7	31	25
H,L= -12 7		
2	117	109
4	25	15
H,L= -11 7		
1	49	-40
3	69	78
5	44	50
13	48	-43
H,L= -10 7		
2	76	-76
4	24	-33
8	67	60
12	33	31
H,L= -9 7		
1	86	70
3	27	-39
5	79	84
9	40	-43
11	49	-42
13	60	54
H,L= -8 7		
4	52	58
6	142	151
10	49	-55
12	45	-52
H,L= -7 7		
1	156	-146
3	77	-64
5	82	-85
7	45	36
9	116	110
11	54	53
13	31	-44

Table 4 (*cont.*)

K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC
H,L=	-6	7	15	31	-21	10	28	16	4	81	-72	2	77	83	H,L=	6	8	5	49	56	4	28	28	7	45	42	10	32	-31
2	146	131	H,L=	0	7	H,L=	7	7	6	113	-111	4	122	-118	0	39	-37	7	56	57	H,L=	5	9	9	35	47	H,L=	-5	11
4	43	34	4	55	-54	3	47	48	10	29	19	6	92	-92	6	30	21	13	28	-24	1	29	-9	H,L=	-2	10	3	45	-38
6	87	-89	6	90	-96	5	27	33	H,L=	-7	8	10	37	41	H,L=	-13	9	H,L=	-4	9	H,L=	-14	10	0	80	76	7	38	30
8	91	-83	8	26	-13	7	29	-28	1	48	55	14	26	6	1	31	12	2	111	-105	4	29	22	6	60	-56	H,L=	-4	11
10	36	35	10	64	76	H,L=	-16	8	3	43	-36	H,L=	-1	8	7	54	-48	4	114	-117	H,L=	-13	10	10	31	4	4	37	-26
12	48	36	14	28	-5	2	24	6	5	86	82	1	112	112	H,L=	-12	9	8	40	42	1	38	-29	H,L=	-1	10	6	39	-35
H,L=	-5	7	H,L=	1	7	H,L=	-14	8	9	55	-59	3	29	28	4	33	31	H,L=	-3	9	5	27	26	1	28	-21	10	31	25
1	212	196	1	132	135	0	77	78	11	27	-28	5	51	-40	8	33	-33	1	47	36	H,L=	-12	10	5	57	49	H,L=	-3	11
3	245	244	3	231	226	H,L=	-13	8	H,L=	-6	8	7	32	-39	H,L=	-11	9	3	57	50	4	27	-12	9	43	-35	3	61	64
5	37	16	5	76	81	3	40	31	0	191	-200	9	29	-30	1	42	-35	7	39	-33	H,L=	-11	10	H,L=	0	10	7	32	-25
7	66	78	7	63	-52	H,L=	-12	8	4	21	3	11	32	-37	3	48	-43	9	58	-58	11	28	-26	0	94	-94	9	30	-19
9	54	-56	9	36	-35	0	56	-62	6	95	95	H,L=	0	8	7	55	51	13	30	21	H,L=	-10	10	2	25	-18	H,L=	-2	11
11	37	-50	13	32	-12	2	24	24	8	26	29	0	170	-166	H,L=	-10	9	H,L=	-2	9	0	50	-46	4	34	16	8	36	24
H,L=	-4	7	H,L=	2	7	4	23	-3	10	29	30	2	58	-61	2	32	-25	2	67	61	H,L=	-9	10	6	32	17	H,L=	-1	11
2	221	-205	4	38	-38	10	38	30	12	26	-30	4	67	59	4	71	-72	4	56	58	1	32	15	H,L=	1	10	3	37	-35
4	52	-50	6	32	34	H,L=	-11	8	H,L=	-5	8	6	113	112	H,L=	-9	9	H,L=	-1	9	3	48	-49	1	44	41	H,L=	0	11
8	102	94	8	51	52	1	35	31	1	25	25	10	28	-1	3	84	76	1	30	-28	H,L=	-8	10	5	34	-37	4	35	34
10	69	79	10	24	4	3	31	30	3	114	117	H,L=	1	8	7	54	-39	3	100	-96	0	40	36	H,L=	2	10	H,L=	-12	12
14	36	-38	14	26	-15	7	34	-37	5	100	-93	3	24	-13	9	35	-31	5	42	-41	4	32	32	0	33	24	0	29	17
H,L=	-3	7	H,L=	3	7	9	64	-65	7	103	-110	11	31	31	11	28	-1	7	27	-34	6	55	-50	H,L=	3	10	6	25	-22
1	41	-25	1	28	-19	11	29	32	11	36	42	H,L=	2	8	H,L=	-8	9	9	61	65	8	29	-30	1	29	-31	H,L=	-6	12
3	146	-147	3	125	-121	H,L=	-10	8	13	29	24	0	63	61	6	30	-10	11	37	33	H,L=	-7	10	3	26	-8	0	47	41
5	101	97	5	45	-43	2	43	-37	H,L=	-4	8	2	57	58	8	37	31	H,L=	0	9	1	88	-78	H,L=	-15	11	4	29	-22
7	88	-91	7	29	18	4	84	80	0	114	120	4	34	46	H,L=	-7	9	2	52	46	3	49	46	3	30	9	H,L=	-5	12
13	36	34	9	29	35	6	43	31	2	25	-31	6	85	-88	1	81	78	8	32	-27	5	58	53	H,L=	-13	11	1	23	15
H,L=	-2	7	H,L=	4	7	H,L=	-12	8	4	95	95	8	29	-33	3	74	-80	12	27	15	H,L=	-6	10	5	26	0	5	24	-13
2	194	182	4	130	125	8	26	-13	8	59	-63	H,L=	3	8	5	87	-90	H,L=	1	9	0	34	-28	H,L=	-10	11	7	47	-16
4	122	123	6	38	40	H,L=	-10	8	10	85	-89	1	74	-68	7	29	-31	3	59	54	2	26	-27	2	28	21	H,L=	-4	12
6	119	133	8	47	-45	10	58	-54	H,L=	-3	8	5	45	45	9	53	49	7	35	33	H,L=	-5	10	8	29	-20	0	39	-29
10	120	-124	10	27	-27	H,L=	-9	8	1	103	-102	7	42	45	13	28	32	9	29	-32	1	77	71	H,L=	-9	11	H,L=	-2	12
12	43	-39	12	28	-11	3	26	-30	3	48	-53	H,L=	4	8	H,L=	-6	9	H,L=	2	9	3	24	-13	1	34	29	4	27	6
H,L=	-1	7	H,L=	5	7	5	33	-27	5	84	80	0	49	49	2	57	44	2	105	-104	5	42	-32	3	49	43	H,L=	-10	13
1	148	-150	7	39	36	7	56	67	7	99	101	2	26	-6	4	73	63	6	26	10	7	49	-47	H,L=	-8	11	4	25	3
3	88	-85	9	34	-5	9	57	62	9	33	39	4	45	-50	6	27	-6	8	28	10	H,L=	-4	10	2	35	-26	H,L=	-9	13
5	37	-39	H,L=	6	7	11	34	-30	11	33	-21	H,L=	5	8	8	92	-83	H,L=	3	9	6	54	48	H,L=	-7	11	5	24	18
7	116	111	4	71	-65	H,L=	-8	8	13	39	-41	1	48	57	10	30	-22	5	30	-18	12	38	-30	1	29	-28			
9	44	37	6	35	-12	0	144	140	H,L=	-2	8	5	42	-40	H,L=	-5	9	H,L=	4	9	H,L=	-3	10	H,L=	-6	11			
11	35	33	8	27	21	2	79	78	0	135	128	7	45	-35	1	86	-83	2	49	50	1	33	-39	4	36	43			

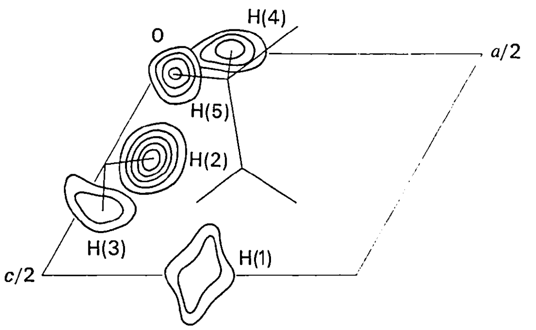

Fig. 2. A composite drawing of the final difference electron-density map, viewed along *b* axis. The contribution of the hydrogen atoms were excluded from the calculated structure factors. Contours are drawn at intervals of 0·1 e.Å^{-3}, beginning with 0·2 e.Å^{-3}.

characteristic of the acid salts, MHX_2, of monocarboxylic acids, HX, belonging to Type *A*. In Type *B* two acidic radicals are crystallographically distinct. Type *A* acid salts are found in several other acids, namely, phenylacetic (Speakman, 1949; Bacon & Curry, 1957, 1960; Manojlović & Speakman, 1968), *p*-hydroxybenzoic (Skinner & Speakman, 1951; Manojlović, 1968), *o*-nitrobenzoic (Shrivastava & Speakman, 1961), acetic (Speakman & Mills, 1961), *p*-chlorobenzoic (Mills & Speakman, 1963), tiifluoroacetic (Golič & Speakman, 1965), aspirin (Manojlović & Speakman, 1967; Sequeira, Berkebile & Hamilton, 1967).

The ammonium ion

The ammonium ion lies on a twofold axis surrounded by oxygen atoms from six different carboxyl groups, making hydrogen bonds with them. The interatomic distances and angles of the ammonium ion and the hydrogen bond are listed in Table 5. The atom H(2) is adjacent to the atom O(2^{iv}), while H(3) is adjacent to O(2^{i}) and O(1).

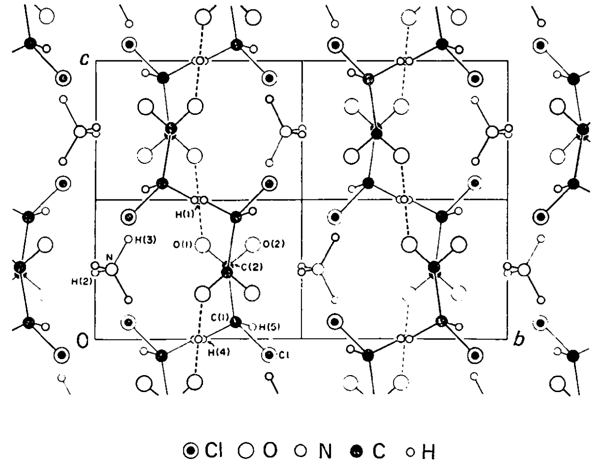

Fig. 3. The structure viewed along *a* axis. The crystallographically symmetrical hydrogen bonds are shown by bioken lines.

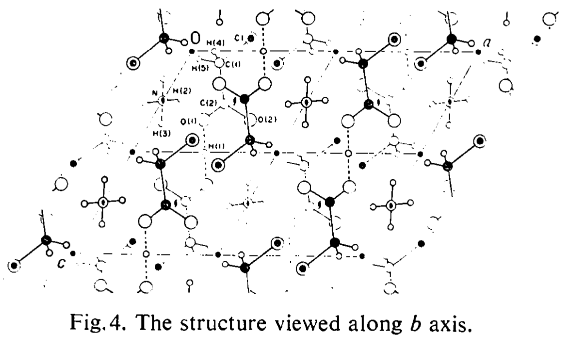

Fig. 4. The structure viewed along *b* axis.

Table 5. *Interatomic distances and bond angles with their standard deviations*

The e.s.d.'s given in parentheses refer to the last figure.

	Ammonium ion		
N—H(2)	1·01 (4) Å	H(2)–N—H(2$^{\mathrm{ii}}$)	110 (4)°
N—H(3)	0·86 (3)	H(2)–N—H(3)	115 (3)
		H(2)–N—H(3$^{\mathrm{ii}}$)	99 (4)
		H(3)–N—H(3$^{\mathrm{ii}}$)	121 (5)
	Chloroacetate residue		
C(1)–Cl	1·768 (4)	Cl—C(1)–C(2)	113·4 (2)
C(1)–C(2)	1·506 (4)	C(1)–C(2)–O(1)	111·4 (2)
C(2)–O(1)	1·278 (4)	C(1)–C(2)–O(2)	123·2 (3)
C(2)–O(2)	1·225 (3)	O(1)–C(2)–O(2)	125·4 (3)
C(1)–H(4)	0·96 (3)	Cl—C(1)–H(4)	104 (3)
C(1)–H(5)	0·99 (5)	H(4)–C(1)–H(5)	111 (3)
		H(5)–C(1)–Cl	109 (2)
		H(4)–C(1)–C(2)	112 (2)
		H(5)–C(1)–C(2)	108 (2)
	Hydrogen bonds		
N ...O(2$^{\mathrm{iv}}$)	2·880 (3)	N—H(2)...O(2$^{\mathrm{iv}}$)	163 (3)
H(2)...O(2$^{\mathrm{iv}}$)	1·90 (4)	N—H(3)...O(2$^{\mathrm{i}}$)	161 (3)
N ...O(2$^{\mathrm{i}}$)	3·148 (3)	N—H(3)...O(1)	108 (3)
H(3)...O(2$^{\mathrm{i}}$)	2·32 (3)		
N ...O(1)	2·926 (4)	C(2)–H(1)...O(1$^{\mathrm{i}}$)	114·8 (3)
H(3)...O(1)	2·55 (4)		
O(1)...O(1$^{\mathrm{i}}$)	2·432 (5)		

Superscripts refer to atoms at:

i $\frac{1}{2}-x,\ \frac{1}{2}-y,\ 1-z$
ii $-x,\ y,\ \frac{1}{2}-z$
iii $-x,\ y,\ -\frac{1}{2}-z$
iv $\frac{1}{2}-x,\ -\frac{1}{2}+y,\ \frac{1}{2}-z$

The chloroacetate residue

The best plane of the carboxyl group and C(1) is represented by the equation

$$-0{\cdot}6279X+0{\cdot}7488Y+0{\cdot}2121Z=2{\cdot}4190,$$

where the direction cosines are referred to the orthogonal axes a, b and c^*, and X, Y and Z are expressed in Å. The deviations of the atoms from the plane are: O(1) 0·003, O(2) 0·004, C(1) 0·003, C(2) −0·010 Å. The Cl atom lies 0·21 Å out of the plane.

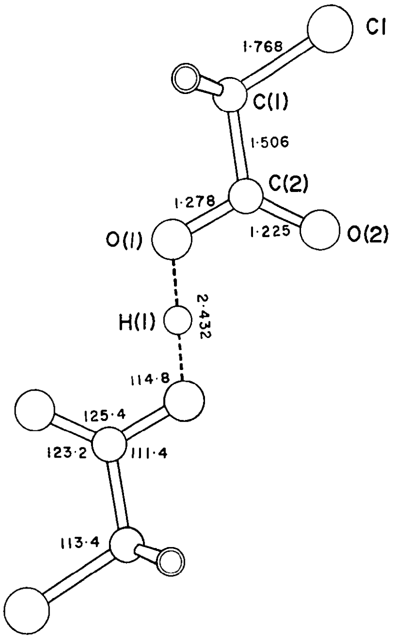

Fig. 5. Bond distances and angles in the chloroacetate residue.

The bond lengths and angles in the chloroacetate residue are presented in Table 5 and Fig. 5. The Cl–C(1) bond length of 1·768 Å is in good agreement with the value of 1·767 Å given by Sutton (1965). The bond length of C(1)–C(2), 1·506 Å, agrees with that found in other Type *A* acid salts and also with that given by Sutton (1965). The C–O bond lengths are 1.278 Å for C(2)–O(1) and 1·225 Å for C(2)–O(2), and the C–C–O angles are 111·4° for C(1)–C(2)–O(1) and 123·2° for C(1)–C(2)–O(2). In the fully ionized carboxyl group the two C–O bond-lengths and the two C–C–O angles are equal, while in the un-ionized carboxyl group they differ (Hahn, 1957). The difference of the bond lengths, 0·053 Å, and the deviation of the angles from 118°, seem to indicate that the carboxyl group in ammonium hydrogen di-chloroacetate is intermediate in character between fully ionized and neutral, as is pointed out in the study of other Type *A* acid salts (Manojlović & Speakman, 1968; Manojlović, 1968). The distance of Cl–Cl$^{\mathrm{iii}}$, 3·604 Å, is nearly equal to the sum of van der Waals radii. There is no abnormal intermolecular contact.

The short hydrogen bond

The chief interest with this compound lies in the crystallographically symmetrical hydrogen bonds, which are shown by broken lines in Figs. 3 and 4. The length O(1)$\cdots$O(1$^{\mathrm{i}}$), is 2·432 (5) Å, in agreement with 2·446 (3) Å which is the weighted mean length of seven Type *A* acid salts (Speakman, 1967). As in most Type *A* acid salts, the symmetry element affecting the hydrogen bond is a centre of symmetry which requires the proton to be exactly at the mid-point between the oxygen atoms. X-ray analysis, however, cannot distinguish the following two cases: (*a*) the case in which the proton vibrates in a symmetrical single-minimum potential well at the mid-point, and (*b*) the case in which it is distributed at random in a set of symmetrical double-minimum wells, situated close to either side of the mid-point. However, even with the neutron diffraction analysis, which is more powerful than the X-ray method for studying the location of hydrogen atoms, it would be difficult to distinguish the two cases.

Meanwhile it is known that the crystals having a very short and possibly symmetrical hydrogen bond show anomalous infrared spectra, although the assignment of each band does not seem to have been sufficiently established. There is a remarkably intense background absorption covering a wide region, of which the maximum lies between 800 and 900 cm^{-1}, with a transmission 'window' in it. The infrared spectrum of ammonium hydrogen di-chloroacetate has been measured at room temperature (Ichikawa, 1970). The expected anomaly was found: the very broad and strong absorption lies in the region of 400–1600 cm^{-1} with its maximum at 900 cm^{-1}.

Judging from the results so far available, which are consistent with other Type *A* acid salts, it seems probable that the O(1)···O(1$^{\text{i}}$) bond is not only crystallographically, but also truly, of the symmetrical single-minimum type. The problem of the symmetrical OHO bond is interesting, since a model of order–disorder type is accepted in most hydrogen-bonded ferroelectrics. Structure analysis in the ferroelectric phase (at about 80°K) is now in progress. A more detailed discussion will be given on the basis of the structures of the para- and ferroelectric phases.

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Barium Aluminate Hydrates. V.* The Crystal Structure of γ-Ba[AlO(OH)$_2$]$_2$

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γ-BaO.Al$_2$O$_3$.2H$_2$O is orthorhombic, *Fdd*2, with $a=20{\cdot}70$, $b=8{\cdot}977$, $c=6{\cdot}416$ Å, $Z=8$. X-ray structural analysis shows that it contains chains of composition [AlO(OH)$_2^{-1}$]$_\infty$, made up of tetrahedra sharing corners. Its formula should therefore be written γ-Ba[AlO(OH)$_2$]$_2$.

Introduction

Carlson & Wells (1948) were the first to produce monobarium aluminate dihydrate and their compound was designated 'α' by Thilo & Gessner (1965) when a second polymorph ('β') was found. Ahmed & Dent Glasser (1970) solved the structure of the α-polymorph and (1971) prepared a third compound of the same empirical formula which they called 'γ'. This present work deals with the γ modification. Crystal data from Ahmed & Dent Glasser (1971) are reproduced in Table 1. The compound crystallizes as plates lying on (100).

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