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A Three-Dimensional X-ray Redetermination of the Crystal Structure of Ammonium Perchlorate

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The crystal structure of ammonium perchlorate has been redetermined by X-ray three-dimensional analysis of 800 reflexions collected with Mo $K\alpha$ monochromatized radiation on an automatic four-circle diffractometer. The cell parameters, redetermined with the same apparatus are: $a=9{\cdot}227$, $b=7{\cdot}454$, $c=5{\cdot}819$ Å (24°C), $Z=4$, space group $Pna2_1$ (C_{2v}^9) from systematic absences and by successful refinement. The previous space group, *Pnma*, used for the two-dimensional analysis, did not allow a three-dimensional refinement. The positional and anisotropic thermal parameters of the non-hydrogen atoms were refined by the least-squares method. An almost spherical distribution of the hydrogen atoms around the nitrogen atom was introduced into the calculation. Final $R=0{\cdot}050$. Residual electron density maxima were observed from difference Fourier syntheses around the nitrogen atom at distances of 0·8–0·9 Å. They make tetrahedral angles to nitrogen and have short H···O distances (2·15–2·50 Å) from eight neighbouring oxygen atoms, indicating that the ammonium ion does not have a completely free rotation.

Introduction

The crystal structure of ammonium perchlorate has been assigned to the orthorhombic space group *Pnma* and studied by X-ray Fourier projections (90 *h*0*l* reflexions with $R=0{\cdot}136$ and 35 *hk*0 reflexions with $R=0{\cdot}128$) by Venkatesan (1957), who suggested an ordered hydrogen-bonded arrangement of the ammonium ion, and from room-temperature single-crystal neutron diffraction by two-dimensional syntheses (120 *h*0*l* and 44 *hk*0 reflexions with weighted $R=0{\cdot}08$) by Smith & Levy (1962) who concluded that the orientation of the ammonium ion is a highly disordered one, the ion undergoing a free or nearly free rotation. A rotating ion is also supported by the infrared spectrum (Waddington, 1958), by heat capacity studies between 5 and 350 K (Justice & Westrum, 1961), by cold neutron studies (Rush, Taylor & Havens, 1961) and by n.m.r. studies (Ibers, 1960; Richards & Shaefer, 1961) at low temperatures. Since only two-dimensional X-ray or neutron diffraction data have been used until now for the crystal structure determination of ammonium perchlorate, we have undertaken the redetermination of this structure by three-dimensional X-ray counter data.

Experimental

An elongated prismatic crystal ($0{\cdot}35\times0{\cdot}40\times0{\cdot}5$ mm) was used for all the measurements. The orientation of the crystal, mounted along the elongated axis, and the analyses of the systematic absences were carried out with Weissenberg and precession photographs. The lattice parameters were determined and the intensities of the reflexions were recorded with Mo $K\alpha$ monochromatized radiation ($\lambda=0{\cdot}71069$ Å) on a Philips PW1100 automatic four-circle diffractometer connected on-line with a computer. The centring of the crystal and the determination of the lattice parameters were automatically performed by means of about 25 strongest reflexions randomly chosen by the diffractometer in a wide region of reciprocal space.

On the basis of the systematic absences two different space groups may be chosen, implying a different orientation of the crystallographic axes: the centrosymmetric space group *Pnma* (D_{2h}^{16}) used by Smith & Levy (1962), by Venkatesan (1957) and by other previous authors (see references therein), and the non-centrosymmetric space group $Pna2_1$ (C_{2v}^9), by permutation of the *b* and *c* axes of the previous orientation.

Independently of the positional parameters given by the authors cited above, we solved the structure by direct methods using the *LSAM* program (Germain, Main & Woolfson, 1971) in the space group *Pnma*. By using 168 reflexions all the non-hydrogen atoms were located and well defined with three-dimensional Fourier syntheses. Furthermore it was impossible to refine the structure in this space group by least-squares methods using all the three-dimensional data, either with the Smith & Levy (1962) parameters or with the new ones, because the reliability index *R*, with an initial value of about 0·27, was unrefinable and divergent.

By using 55 *hk*0 reflexions in the *Pnma* group orientation the structure was refinable with isotropic temperature factors for non-hydrogen atoms to a reliability index $R=0{\cdot}07$ and x,y positional parameters very close to the values given by Smith & Levy (1962). It was therefore evident that the centrosymmetric space group *Pnma* is incorrect.

The refinement was then performed in the space group $Pna2_1$ and converged very rapidly to reliable values of the index R, the anisotropic parameters and the interatomic distances and angles.

Crystal data

Ammonium perchlorate, NH_4ClO_4. Orthorhombic pyramidal; space group $Pna2_1$ (C_{2v}^9, No. 33) from systematic absences ($0kl$, $k+l=2n+1$; $h0l$, $h=2n+1$) and by successful refinement. $a=9{\cdot}227$, $b=7{\cdot}454$, $c=5{\cdot}819$ Å, at 24°C. $V=400{\cdot}2$ Å^3, F.W. 145·50, $Z=4$, $F(000)=296$. $D_c=2{\cdot}415$ g cm^{-1}. In this orientation the crystals are elongated along the b axis.

The X-ray intensities were corrected for Lorentz and polarization factors; only the values of $F_o > 1{\cdot}5\sigma(F_o)$ were used for the calculations. From a Wilson plot of the data overall scale and temperature factors were obtained. The positional parameters, the isotropic and anisotropic thermal parameters of the non-hydrogen atoms and the scale factors (K) for each hkl layer were then refined by the least-squares method using the program *MIQUAD* of Immirzi (1967*a*) until convergence of the R value at 0·055. The atomic scattering factors given by Hanson, Herman, Lea & Skillmann (1964) were used.

102 fractional (0·039 H) hydrogen atoms (hydrogenoids) were then introduced into the calculation with the isotropic temperature factor ($B=4{\cdot}30$) of the nitrogen atom and located in equidistant and symmetrical positions around the nitrogen atom on a sphere of radius 1·03 Å, at a distance of about 0·35 Å from each other. With this distribution the hydrogenoids are regularly interpenetrated, giving an almost spherical electron distribution. The weights of the reflexions were calculated with the formula $1/w=\sigma^2+0{\cdot}004\ F_o^2$ (Gilmore & Woodward, 1971).

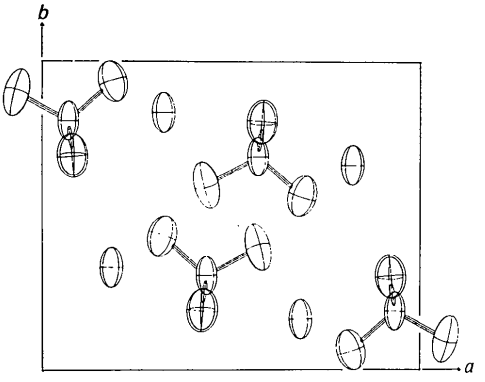

Fig. 1. Orthographic projection of the unit cell on the xy plane. *ORTEP* plot of thermal ellipsoids scaled to include 50% probability.

The positional and thermal parameters of the non-hydrogen atoms were refined until the reliability index converged to a final R value = 0·050, the fitting to 1·02 and the variation of the positional and anisotropic temperature factors of the non-hydrogen atoms were of the same order as their standard deviations. Two different distributions of hydrogen atoms gave identical values of R and of interatomic distances and angles. The final positional and thermal parameters of the non-hydrogen atoms are given in Table 1, the observed and calculated structure factors in Table 2 and the interatomic distances and angles in Table 3. An orthographic xy projection of the unit cell (Fig. 1) and an xz projection of the perchlorate ion thermal ellipsoids (Fig. 2) were plotted with the *ORTEP* program of Johnson (1965).

Three-dimensional difference Fourier syntheses, using structure factors not including the contribution of the hydrogen atoms, were calculated with the *FOUR* 3*D* program of Immirzi (1967*b*) in the regions occupied by the perchlorate and the ammonium ions. Residual electron density maxima were observed around the nitrogen atom (Fig. 3, Table 4). Four of these correspond to a fixed position of the ammonium ion. By using the hydrogen atoms in these fixed positions for the refinement, the same convergent reliability index $R=0{\cdot}050$ was obtained, with a fitting of 1·07. The interatomic distances and angles are given in square brackets in Table 3.

Results and discussion

The assignment of ammonium perchlorate to the centrosymmetric space group *Pnma* seems to have been based on the fact that from morphological studies the crystal was considered to belong to the orthorhombic bipyramidal class (Venkatesan, 1957). Consequently chlorine, nitrogen and two oxygen atoms were located, in the *Pnma* group, in a special position with $y=\pm 0{\cdot}250$, the other two oxygen atoms being specularly symmetrical with respect to a symmetry plane normal to the y axis at $y=0{\cdot}250$.

Table 1. *Fractional coordinates and thermal parameters*

Coordinates are $\times 10^5$. Thermal parameters are defined by
$T=\exp[-\frac{1}{4}(B_{11}a^{*2}h^2+B_{22}b^{*2}k^2+B_{33}c^{*2}l^2+2B_{12}a^*b^*hk+2B_{13}a^*c^*hl+2B_{23}b^*c^*kl)\times 10^{-3}]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl	43199 (5)	30821 (6)	25082 (33)	2090 (15)	7247 (15)	2115 (16)	−110 (11)	92 (46)	211 (34)
O(1)	42064 (31)	19487 (36)	45055 (45)	4632 (134)	9190 (108)	1678 (79)	389 (79)	−178 (72)	487 (66)
O(2)	42004 (26)	19770 (31)	4628 (55)	3207 (88)	8271 (88)	3525 (115)	132 (58)	−40 (74)	−905 (77)
O(3)	56815 (20)	39857 (41)	25745 (93)	3359 (78)	10618 (114)	5627 (142)	−1990 (73)	656 (158)	−790 (278)
O(4)	31487 (23)	43483 (26)	24550 (63)	4179 (77)	7993 (64)	4136 (92)	1116 (58)	−1223 (145)	−42 (137)
N	18094 (22)	33411 (25)	−24876 (87)	2505 (66)	7819 (67)	3109 (83)	116 (51)	−1108 (164)	56 (173)

Table 2. *Observed and calculated structure factors* (×10)

H	K	L	FO	FC
2	0	0	446	468
12	0	0	99	92
8	0	1	47	44
2	0	2	29	26
14	0	2	40	41
6	0	3	149	147
4	0	4	79	75
12	0	5	39	36
2	0	5	330	318
8	0	6	140	138
0	0	8	93	84
13	1	0	22	22
7	1	0	120	116
1	1	0	286	268
4	1	1	87	85
9	1	1	29	25
14	1	1	77	75
9	1	2	69	70
3	1	2	14	17
2	1	3	161	157
8	1	3	116	112
14	1	3	55	54
8	1	4	61	57
3	1	4	16	17
2	1	5	220	215
7	1	5	14	15
10	1	6	50	49
5	1	6	24	18
0	1	7	54	56
6	1	7	52	53
5	1	8	20	21
2	1	9	46	45
3	2	0	232	200
8	2	0	164	156
13	2	0	18	15
10	2	1	103	101
5	2	1	10	12
0	2	2	36	29
5	2	2	68	71
10	2	2	39	41
12	2	3	54	50
6	2	3	77	76
1	2	3	456	441
4	2	4	40	41
9	2	4	57	59
11	2	5	14	10
6	2	5	65	65
1	2	5	112	103
4	2	6	19	18
9	2	6	41	39
6	2	7	28	31
0	2	8	38	36
6	2	8	18	23
11	3	0	35	36
6	3	0	65	63
0	3	1	85	72
5	3	1	186	189
10	3	1	21	22
14	3	2	12	11
7	3	2	202	204
1	3	2	346	350
4	3	3	19	13
10	3	3	22	22
10	3	4	37	39
5	3	4	101	103
0	3	5	60	63
5	3	5	78	80
10	3	6	18	20
4	3	6	70	73
2	3	7	20	18
9	3	7	29	27
0	3	9	23	24
3	4	0	101	100
9	4	0	28	28
12	4	1	21	20
6	4	1	11	5
1	4	1	108	111
4	4	2	12	16
9	4	2	82	85
12	4	3	16	14
5	4	3	123	124
0	4	4	14	16
5	4	4	96	96
11	4	4	51	54
3	4	5	24	24
3	4	6	76	75
7	4	7	54	55
1	4	8	32	31
11	5	0	21	19
6	5	0	7	8
1	5	0	15	16
4	5	1	8	10
11	5	1	59	57
9	5	2	40	40
2	5	2	34	35
3	5	3	183	186
9	5	3	48	47
9	5	4	29	29
2	5	4	16	17
5	5	5	48	49
5	5	6	28	30
1	5	7	23	24
4	5	8	14	12
2	6	0	42	39
7	6	0	22	22
12	6	1	16	16
5	6	1	7	9
0	6	2	28	25
5	6	2	61	62
10	6	2	8	7
9	6	3	29	31
3	6	3	8	9
2	6	4	19	19
7	6	4	11	12
9	6	5	18	18
2	6	5	42	40
3	6	6	31	31
8	6	6	17	17
1	6	7	35	36
9	7	0	19	19
4	7	0	75	73
1	7	1	34	33
6	7	1	31	32
11	7	1	8	9
6	7	2	15	16
1	7	2	53	53
5	7	3	17	17
10	7	3	9	10
7	7	4	15	15
1	7	4	21	22
5	7	5	4	5
7	7	6	11	12
0	7	7	10	11
1	8	0	7	7
6	8	0	21	20
8	8	1	7	7
3	8	1	9	9
3	8	2	7	8
10	8	2	6	6
5	8	3	7	7
0	8	4	33	33
6	8	4	11	12
2	8	5	25	24
4	8	6	3	3
2	9	0	20	20
6	9	1	12	12
4	9	2	8	9
3	9	3	4	4
4	9	4	10	11
3	9	5	2	2
1	10	0	5	5
7	10	0	2	2
4	10	1	9	9
2	10	2	5	5
4	10	3	5	6
2	10	4	5	5
6	11	0	1	1
1	11	0	2	2
5	11	1	2	2
1	11	2	3	3

H	K	L	FO	FC
4	0	0	297	275
14	0	0	68	66
6	0	1	219	217
6	0	2	31	28
14	0	3	31	26
4	0	3	140	132
6	0	4	163	155
10	0	5	132	125
0	0	6	298	277
10	0	6	21	22
2	0	8	26	25
12	1	0	99	97
6	1	0	143	135
0	1	1	590	678
5	1	1	32	29
10	1	1	62	61
14	1	2	23	24
7	1	2	167	166
2	1	2	111	86
3	1	3	81	76
9	1	3	45	44
13	1	4	21	18
7	1	4	83	83
2	1	4	186	186
3	1	5	15	11
8	1	5	128	126
9	1	6	21	24
4	1	6	153	149
1	1	7	28	27
8	1	7	43	44
4	1	8	55	53
3	1	9	18	16
4	2	0	140	130
9	2	0	50	49
14	2	0	47	45
9	2	1	128	129
4	2	1	370	369
1	2	2	367	348
6	2	2	57	51
11	2	2	57	58
11	2	3	38	37
5	2	3	85	84
0	2	4	203	195
5	2	4	34	30
10	2	4	24	25
10	2	5	72	72
5	2	5	16	21
0	2	6	114	110
5	2	6	32	32
10	2	6	20	20
5	2	7	32	31
1	2	8	48	45
2	2	9	41	39
10	3	0	72	70
5	3	0	109	107
1	3	1	109	95
6	3	1	92	88
11	3	1	62	66
13	3	2	59	59
6	3	2	36	35
0	3	3	117	106
5	3	3	203	208
11	3	3	70	71
9	3	4	42	42
4	3	4	159	166
1	3	5	22	27
6	3	5	64	71
9	3	6	27	28
3	3	6	52	53
3	3	7	101	101
5	3	8	48	47
2	3	9	18	19
5	4	0	122	117
10	4	0	13	13
10	4	1	15	15
5	4	1	79	76
0	4	2	113	102
5	4	2	190	196
10	4	2	10	12
11	4	3	14	16
4	4	3	55	55
1	4	4	47	44
6	4	4	14	15
9	4	5	41	42
2	4	5	17	19
4	4	6	9	6
5	4	7	45	44
3	4	8	61	62
10	5	0	8	6
5	5	0	25	24
0	5	1	41	41
5	5	1	120	120
13	5	1	30	28
7	5	2	87	88
1	5	2	147	145
5	5	3	123	123
10	5	3	9	8
7	5	4	41	42
1	5	4	53	49
6	5	5	35	36
4	5	6	39	38
2	5	7	19	17
3	5	8	12	14
3	6	0	42	37
8	6	0	29	30
10	6	1	32	32
4	6	1	68	67
1	6	2	69	70
6	6	2	12	13
11	6	2	34	34
7	6	3	46	48
2	6	3	31	30
3	6	4	41	41
8	6	4	19	21
8	6	5	7	8
1	6	5	21	22
4	6	6	8	9
5	6	7	16	16
0	6	8	9	10
8	7	0	17	17
3	7	0	9	10
2	7	1	37	36
7	7	1	13	13
12	7	1	5	6
5	7	2	5	6
0	7	3	16	15
6	7	3	16	17
11	7	3	11	10
6	7	4	11	12
0	7	5	34	33
6	7	5	25	25
6	7	6	8	9
1	7	7	11	11
2	8	0	21	20
8	8	0	27	27
7	8	1	9	8
2	8	1	39	38
5	8	2	9	9
10	8	3	12	12
4	8	3	11	12
1	8	4	4	4
8	8	4	17	17
0	8	6	22	21
5	8	6	4	4
0	9	1	23	23
8	9	1	13	13
3	9	2	2	1
6	9	3	6	7
2	9	4	11	11
4	9	5	2	2
2	10	0	9	8
8	10	0	5	5
2	10	1	4	4
3	10	2	3	3
2	10	3	2	2
3	10	4	3	3
5	11	0	1	1
0	11	1	3	3
5	11	2	2	2
0	11	3	2	2

H	K	L	FO	FC
6	0	0	403	395
14	0	1	23	21
4	0	1	13	15
8	0	2	280	274
12	0	3	37	37
2	0	3	163	160
8	0	4	245	237
8	0	5	61	57
2	0	6	95	90
6	0	7	62	59
6	0	8	25	23
10	1	0	141	135
4	1	0	586	626
1	1	1	64	58
6	1	1	366	355
11	1	1	20	18
13	1	2	33	30
6	1	2	85	83
1	1	2	426	412
4	1	3	28	29
10	1	3	63	63
12	1	4	66	67
6	1	4	80	80
1	1	4	152	137
4	1	5	62	60
10	1	5	30	32
8	1	6	32	33
3	1	6	13	14
2	1	7	61	56
9	1	7	18	19
2	1	8	27	28
0	2	0	483	635
5	2	0	87	75
10	2	0	27	24
13	2	1	28	29
8	2	1	47	45
3	2	1	137	121
2	2	2	52	62
7	2	2	68	70
13	2	2	13	9
10	2	3	57	56
4	2	3	126	128
1	2	4	134	125
6	2	4	127	126
11	2	4	33	38
9	2	5	63	64
4	2	5	192	192
1	2	6	69	66
6	2	6	66	68
11	2	6	25	27
4	2	7	46	44
2	2	8	25	25
1	2	9	36	36
9	3	0	51	50
4	3	0	406	407
2	3	1	125	126
7	3	1	19	21
12	3	1	12	11
12	3	2	43	44
5	3	2	249	256
1	3	3	54	51
6	3	3	31	31
13	3	3	39	39
8	3	4	25	23
3	3	4	99	101
2	3	5	74	77
8	3	5	28	29
7	3	6	58	62
2	3	6	34	36
5	3	7	74	74
4	3	8	24	27
0	4	0	60	51
6	4	0	13	12
11	4	0	66	67
9	4	1	64	63
4	4	1	107	102
1	4	2	138	133
6	4	2	16	18
11	4	2	80	84
10	4	3	9	7
3	4	3	48	51
2	4	4	22	24
7	4	4	26	27
7	4	5	39	42
1	4	5	45	42
5	4	6	56	58
3	4	7	15	16
5	4	8	39	41
9	5	0	35	33
4	5	0	107	109
1	5	1	22	22
6	5	1	73	74
13	5	2	28	28
5	5	2	105	107
0	5	3	37	41
6	5	3	46	46
11	5	3	56	55
5	5	4	40	41
2	5	5	35	34
9	5	5	8	11
3	5	6	25	24
3	5	7	64	65
1	5	8	38	39
4	6	0	25	25
9	6	0	21	20
9	6	1	33	33
3	6	1	7	4
2	6	2	18	17
7	6	2	16	8
12	6	2	7	9
6	6	3	21	22
1	6	3	85	84
4	6	4	11	11
9	6	4	16	18
7	6	5	17	17
0	6	6	35	34
5	6	6	21	22
4	6	7	15	14
1	6	8	13	12
7	7	0	18	17
2	7	0	61	58
3	7	1	17	16
8	7	1	19	20
10	7	2	16	16
4	7	2	42	43
1	7	3	33	32
7	7	3	8	9
10	7	4	16	15
5	7	4	4	5
1	7	5	11	12
7	7	5	8	8
4	7	6	28	27
2	7	7	12	10
3	8	0	3	2
10	8	0	4	4
6	8	1	17	17
1	8	1	7	6
6	8	2	6	7
8	8	3	3	2
3	8	3	7	8
2	8	4	12	12
6	8	5	9	10
1	8	6	4	1
8	9	0	7	6
2	9	1	12	12
8	9	2	2	2
2	9	2	9	9
8	9	3	9	9
1	9	4	3	2
5	9	5	2	2
3	10	0	3	3
8	10	1	2	2
1	10	1	5	5
5	10	2	2	2
1	10	3	5	5
5	10	4	1	2
4	11	0	3	3
1	11	1	1	1
4	11	2	1	2
1	11	3	1	1

H	K	L	FO	FC
8	0	0	455	447
12	0	1	49	48
2	0	1	619	734
10	0	2	56	58
10	0	3	110	103
0	0	4	595	604
10	0	4	28	30
6	0	5	122	119
4	0	6	34	33
4	0	7	25	28
4	0	9	46	48
9	1	0	74	74
3	1	0	13	12
2	1	1	480	535
7	1	1	28	30
12	1	1	43	42
12	1	2	78	77
5	1	2	95	97
0	1	3	125	133
5	1	3	42	43
11	1	3	25	28
10	1	4	75	76
5	1	4	30	28
0	1	5	338	327
5	1	5	16	20
11	1	5	23	15
7	1	6	45	45
2	1	6	106	102
3	1	7	44	44
7	1	8	31	31
1	1	8	42	43
1	2	0	271	257
6	2	0	300	285
11	2	0	34	35
12	2	1	69	67
7	2	1	197	197
2	2	1	305	307
3	2	2	165	170
8	2	2	73	68
14	2	2	30	28
9	2	3	108	108
3	2	3	49	49
2	2	4	136	137
7	2	4	66	64
12	2	4	26	27
8	2	5	41	42
3	2	5	20	24
2	2	6	72	73
7	2	6	34	35
9	2	7	37	38
2	2	7	30	31
3	2	8	56	56
13	3	0	41	43
8	3	0	52	52
3	3	0	213	203
3	3	1	169	179
8	3	1	15	9
13	3	1	48	50
10	3	2	31	29
4	3	2	175	177
2	3	3	42	43
7	3	3	37	38
12	3	4	33	35
7	3	4	97	99
2	3	4	79	83
3	3	5	60	57
10	3	5	12	13
6	3	6	18	20
1	3	6	69	70
7	3	7	16	13
3	3	8	30	28
1	4	0	8	6
7	4	0	51	53
13	4	0	34	36
8	4	1	13	11
3	4	1	59	59
2	4	2	10	9
7	4	2	12	11
13	4	2	25	28
9	4	3	62	63
2	4	3	11	14
3	4	4	122	121
9	4	4	36	39
5	4	5	16	17
0	4	6	18	15
7	4	6	16	16
2	4	7	10	4
13	5	0	14	17
8	5	0	13	14
3	5	0	63	60
2	5	1	81	79
8	5	1	11	12
12	5	2	20	21
4	5	2	82	85
1	5	3	59	58
7	5	3	8	9
11	5	4	11	9
4	5	4	51	53
3	5	5	49	50
9	5	6	18	20
2	5	6	7	6
5	5	7	44	45
0	6	0	72	69
5	6	0	34	30
11	6	0	28	27
7	6	1	36	36
2	6	1	66	64
3	6	2	103	107
8	6	2	21	22
12	6	3	12	13
5	6	3	29	30
0	6	4	39	37
5	6	4	30	31
11	6	4	20	21
6	6	5	15	15
1	6	6	17	18
6	6	6	16	16
3	6	7	7	6
12	7	0	18	18
6	7	0	18	18
1	7	0	26	24
4	7	1	9	9
9	7	1	18	17
9	7	2	19	20
3	7	2	4	5
2	7	3	21	20
8	7	3	13	13
9	7	4	13	13
4	7	4	40	40
2	7	5	26	25
8	7	5	15	15
2	7	6	19	20
3	7	7	13	14
4	8	0	9	9
11	8	1	3	4
5	8	1	6	6
0	8	2	32	32
7	8	2	3	4
7	8	3	8	8
2	8	3	21	21
4	8	4	4	4
4	8	5	18	18
2	8	6	9	9
6	9	0	9	9
3	9	1	4	4
7	9	2	2	1
0	9	3	13	13
6	9	4	6	6
0	9	5	16	16
2	9	6	7	7
5	10	0	2	2
7	10	1	3	3
0	10	2	4	4
6	10	2	5	5
0	10	4	6	6
2	10	5	4	4
3	11	0	2	2
2	11	1	2	2
3	11	2	2	1
2	11	3	1	1

H	K	L	FO	FC
10	0	0	32	33
10	0	1	184	176
0	0	2	686	758
12	0	2	40	35
8	0	3	23	26
2	0	4	163	155
12	0	4	54	49
4	0	5	176	167
6	0	6	93	90
2	0	7	75	67
2	0	9	71	65
8	1	0	140	130
2	1	0	517	554
3	1	1	84	72
8	1	1	215	207
13	1	1	14	14
10	1	2	43	44
4	1	2	92	91
1	1	3	121	115
6	1	3	137	135
13	1	3	17	13
9	1	4	45	45
4	1	4	248	248
1	1	5	21	18
6	1	5	216	211
12	1	5	35	33
6	1	6	54	55
1	1	6	64	59
5	1	7	30	31
6	1	8	27	26
0	1	9	64	64
2	2	0	373	374
7	2	0	134	136
12	2	0	52	50
11	2	1	33	29
6	2	1	121	117
1	2	1	453	507
4	2	2	24	26
9	2	2	112	112
13	2	3	31	33
7	2	3	206	205
2	2	3	43	45
3	2	4	44	38
8	2	4	96	93
12	2	5	40	40
7	2	5	73	73
2	2	5	177	173
3	2	6	45	43
8	2	6	60	60
7	2	7	69	68
1	2	7	110	106
5	2	8	37	35
12	3	0	56	56
7	3	0	105	98
2	3	0	246	234
4	3	1	17	15
9	3	1	21	22
14	3	1	19	19
9	3	2	58	59
3	3	2	172	175
3	3	3	281	286
9	3	3	57	59
11	3	4	20	18
6	3	4	33	34
1	3	4	120	110
4	3	5	20	20
11	3	5	33	36
5	3	6	60	60
1	3	7	29	29
8	3	7	12	8
1	3	8	64	67
2	4	0	40	35
8	4	0	12	14
13	4	1	28	31
7	4	1	93	90
2	4	1	45	44
3	4	2	298	316
8	4	2	24	26
13	4	3	33	35
7	4	3	125	128
1	4	3	221	214
4	4	4	8	5
10	4	4	10	9
4	4	5	42	44
1	4	6	34	33
9	4	6	28	28
1	4	7	83	83
12	5	0	20	22
7	5	0	26	24
2	5	0	35	30
3	5	1	158	156
9	5	1	35	34
10	5	2	8	6
3	5	2	62	63
2	5	3	49	49
8	5	3	11	11
10	5	4	9	5
3	5	4	41	40
4	5	5	8	6
7	5	6	31	33
1	5	6	42	43
6	5	7	19	17
1	6	0	34	34
6	6	0	38	36
12	6	0	14	15
6	6	1	27	28
1	6	1	59	58
4	6	2	7	8
9	6	2	40	41
10	6	3	20	22
4	6	3	33	34
1	6	4	28	27
6	6	4	17	17
10	6	5	19	21
4	6	5	37	37
2	6	6	18	17
7	6	6	6	6
2	6	7	15	15
10	7	0	27	26
5	7	0	14	15
0	7	1	41	41
5	7	1	11	10
10	7	1	10	9
7	7	2	31	31
2	7	2	24	24
3	7	3	26	27
9	7	3	19	18
8	7	4	9	8
2	7	4	29	28
4	7	5	7	8
9	7	5	7	7
1	7	6	17	18
0	8	0	59	59
5	8	0	5	4
10	8	1	18	19
4	8	1	24	23
2	8	2	9	8
8	8	2	20	20
6	8	3	13	13
1	8	3	7	8
5	8	4	3	4
3	8	5	5	4
3	8	6	3	4
4	9	0	18	18
5	9	1	2	3
6	9	2	8	7
2	9	3	7	7
5	9	4	2	2
2	9	5	8	8
0	10	0	10	9
6	10	0	9	9
6	10	1	3	3
1	10	2	5	5
6	10	3	2	2
1	10	4	3	3
1	10	5	3	3
2	11	0	3	3
3	11	1	3	3
2	11	2	1	1
3	11	3	3	3

The new x,y,z coordinates found in this work by using the non-centrosymmetric space group $Pna2_1$ may be transformed into the x',y',z' coordinates corresponding to those found by Venkatesan (1957) and Smith & Levy (1962) using the equivalences: $x'=x$, $y'=z$, $z'=\frac{1}{2}-y$. These new parameters differ from those found by Smith & Levy (1962) by an average value of $\pm 0{\cdot}003$, a little greater than the standard deviations given by these authors (0·001–0·002). Also the deviations of the new y' values from $\pm 0{\cdot}250$ are very small (Cl $+0{\cdot}001$, O(3) $-0{\cdot}004$, O(4) $+0{\cdot}007$, N $+0{\cdot}001$) and the difference $0{\cdot}500-y'[\mathrm{O}(2)]-y'[\mathrm{O}(3)]=0{\cdot}003$. It is likely that such small deviations from the conditions of centrosymmetry do not sensibly affect the morphology of the crystal and thc description of the structure as centrosymmetric by using few reflexions either in the case of two-dimensional analysis (Venkatesan, 1957; Smith & Levy, 1962), or in the case of direct method determination with 168 three-dimensional strong reflexions (present work). For reasons of symmetry the structure is refinable on $hk0$ and $h0l$ projection in the $Pnma$ space group.

The Cl–O distances (Table 3) show differences which in part may be due to the imperfect localization of the hydrogen atoms, because of their statistical disorder, but as the N···O distances indicate hydrogen interactions between ammonium and perchlorate ions, it is

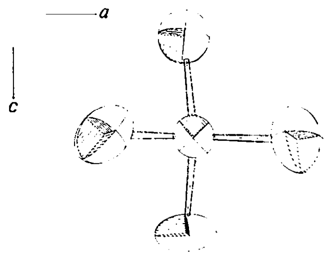

Fig. 2. Perchlorate ion projection on the xz plane. *ORTEP* plot of thermal ellipsoids scaled to include 50% probability.

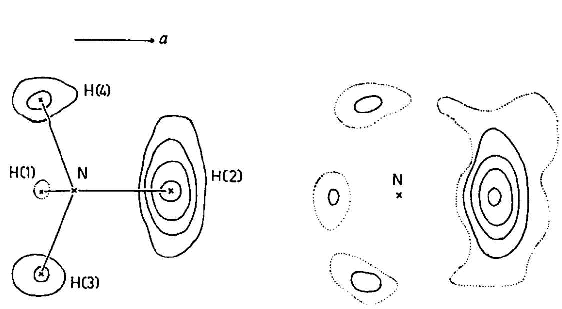

Fig. 3. Residual electron densities around the nitrogen atom: (right) in the xz section through the centre of the nitrogen atom; (left) composite drawing with sections through the centre of the hypothetical fractional hydrogen atoms (Table 4). Dotted lines at 0·8 e Å^{-3}; line intervals of 0·05 e Å^{-3}.

Table 3. *Interatomic distances* (Å) *and angles* (°) *and their e.s.d.'s*

In square brackets are given the bond distances and angles obtained with a fixed position of the ammonium ions.

Bond distances

Cl–O(1)	1·441 (3) [1·444 (3)]	Cl–O(3)	1·426 (2) [1·424 (2)]
Cl–O(2)	1·452 (3) [1·441 (4)]	Cl–O(4)	1·435 (2) [1·435 (2)]

Cl–O Average 1·438 [1·436]

Other distances

N–O(2) [4]	2·97	N–O(2) [3]	3·10
N–O(2) [1]	2·98	N–O(4) [1]	3·22
N–O(4) [6]	2·98	N–O(4) [2]	3·28
N–O(1) [5]	2·98	N–O(3) [5]	3·51
N–O(1) [2]	3·01	N–O(3) [4]	3·57
N–O(1) [3]	3·08	N–O(3) [6]	3·98

Bond angles

O(1)–Cl–O(2)	108·8 (1) [108·7 (1)]	O(2)–Cl–O(3)	110·9 (1) [110·6 (1)]
O(1)–Cl–O(3)	108·6 (1) [108·7 (1)]	O(2)–Cl–O(4)	107·4 (1) [107·4 (1)]
O(1)–Cl–O(4)	110·4 (1) [110·4 (1)]	O(3)–Cl–O(4)	110·7 (1) [111·1 (1)]

O–Cl–O Average 109·5 [109·5]

Other angles

O(2) [3]–N–O(3) [4]	130·8	O(4) [2]–N–O(1) [3]	104·7
O(1) [3]–N–O(3) [5]	130·5	O(2) [1]–N–O(2) [4]	103·9
O(4) [1]–N–O(4) [2]	127·1	O(4) [1]–N–O(4) [6]	103·8
O(1) [2]–N–O(3) [4]	121·8	O(1) [2]–N–O(1) [5]	103·1
O(2) [1]–N–O(3) [5]	121·5	O(4) [2]–N–O(4) [6]	102·4
O(3) [4]–N–O(3) [5]	110·4	O(1) [5]–N–O(3) [4]	102·4
O(1) [2]–N–O(4) [1]	108·6	O(2) [4]–N–O(3) [5]	101·2
O(2) [1]–N–O(4) [2]	108·5	O(2) [3]–N–O(2) [4]	92·8
O(2) [1]–N–O(1) [3]	107·9	O(1) [3]–N–O(1) [5]	92·2
O(1) [2]–N–O(2) [3]	107·4	O(3) [5]–N–O(2) [3]	91·6
O(4) [1]–N–O(2) [3]	104·8	O(3) [4]–N–O(1) [3]	91·4

Asymmetric units

[1]	x	y	z	[4]	$x-\frac{1}{2}$	$\frac{1}{2}-y$	z
[2]	x	y	$z-1$	[5]	$x-\frac{1}{2}$	$\frac{1}{2}-y$	$z-1$
[3]	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$z-\frac{1}{2}$	[6]	$\frac{1}{2}-x$	$y-\frac{1}{2}$	$z-\frac{1}{2}$

Table 4. *Residual electron density maxima around the nitrogen atom located in a tetrahedral configuration, corresponding to hypothetical fractional hydrogen atoms: fractional coordinates* ($\times 10^3$), N–H *distances* (Å), H–N–H *angles* (°) *and* H···O *distances* (Å)

	x	y	z	e Å^{-3}	N–H
H(1)	150	220	−245	0·8	0·90
H(2)	273	350	−250	1·0	0·86
H(3)	150	375	−125	0·9	0·83
H(4)	146	375	−378	0·9	0·87

H(1)–N–H(2)	116·5	H(2)–N–H(3)	107·2
H(1)–N–H(3)	102·5	H(2)–N–H(4)	108·1
H(1)–N–H(4)	103·6	H(3)–N–H(4)	119·4

H(1)···O(4) [6]	2·15	H(3)···O(1) [3]	2·51
H(1)···O(2) [4]	2·78	H(3)···O(2) [4]	2·41
H(1)···O(1) [5]	2·83	H(3)···O(4) [1]	2·68
H(2)···O(1) [2]	2·50	H(4)···O(1) [5]	2·36
H(2)···O(2) [1]	2·47	H(4)···O(2) [3]	2·52

likely that the Cl–O distance is also influenced by the strength of the O···HN bonds. The multiplicity of the O···N short contacts (Table 3) confirms a statistically dynamic orientation of the ammonium ion around the nitrogen atomic position. However, many O···N···O angles (Table 3) near to the tetrahedral value seem to indicate that some positions of the ammonium ion could be more favoured.

The three-dimensional difference Fourier syntheses show residual positive electron densities of 0·4–0·5 e Å^{-3} in the positions occupied by chlorine and oxygen atoms and of 0·6–0·7 e Å^{-3} in the positions of their close neighbours. Definite maxima of greater electron densities (0·8–1·0 e Å^{-3}) are observed around the nitrogen atom at a distance of about 0·8–0·9 Å, that is in the region occupied by the cloud of hydrogen atoms. Fig. 3 shows (right) the maxima appearing in the *xz* section through the *y* position of nitrogen atom, and (left) four maxima located in an almost tetrahedral position around the nitrogen atom.

As shown by the N–H distances and angles (Table 4), they may reasonably be interpreted as fractional hydrogen atoms corresponding to a favoured orientation of the ammonium ion. All these 'hydrogenoids' have at least two short H···O distances from neighbouring oxygen atoms. All these H···O distances are almost equivalent and seem to indicate that this favoured position corresponds to a rather equilibrated orientation of the ammonium ion with each hydrogen located 'between' two oxygen atoms. These contacts involve all the eight oxygen atoms with the shortest O···N distances (Table 3).

The presence of other maxima and the elongated form of the maximum 'H(2)', which may be due to a superposition of several 'hydrogenoids' could indicate

that other favoured orientations of the ammonium ion may be present in this structure. In any case it seems reasonable to conclude that the rotation of the ammonium ion is not completely free, the distribution of oxygen atoms around the nitrogen atom imposing a certain number of preferential orientations, as that described above.

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References

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

GILMORE, C. J. & WOODWARD, P. (1971). *J. Chem. Soc.* (*A*), pp. 3453–3458.

HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.

IBERS, J. A. (1960). *J. Chem. Phys.* **32**, 1448–1449.

IMMIRZI, A. (1967*a*). *Ric. Sci.* **37**, 743–749.

IMMIRZI, A. (1967*b*). *Ric. Sci.* **37**, 846–854.

JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.

JUSTICE, B. H. & WESTRUM, E. F. JR (1961). St Louis Meeting, American Chemical Society.

RICHARDS, R. E. & SHAEFER, T. (1961). *Trans. Faraday Soc.* **57**, 210–222.

RUSH, J. J., TAYLOR, T. I. & HAVENS, W. W. JR (1961). *Bull. Amer. Phys. Soc. Ser.* II, No. 3, **6**, 261, L6.

SMITH, H. G. & LEVY, H. A. (1962). *Acta Cryst.* **15**, 1201–1204.

VENKATESAN, K. (1957). *Proc. Indian Acad. Sci.* A**46**, 134–142.

WADDINGTON, T. C. (1958). *J. Chem. Soc.* pp. 4340–4344.

Acta Cryst. (1975). B**31**, 2056

The Crystal Structure of *trans*-1-Amino-1,3-dicarboxycyclopentane

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trans-1-Amino-1,3-dicarboxycyclopentane crystallizes with acetic acid of crystallization in the space group $Pca2_1$, with $Z=4$, $a=9{\cdot}122$ (5), $b=13{\cdot}964$ (9), $c=8{\cdot}667$ (5) Å, $V=1104$ (1) Å^3. $D_x=1{\cdot}40$ and $D_m=1{\cdot}39$ g cm^{-3}. Diffractometer data, collected with monochromatic Cu $K\alpha$ radiation, consisted of 1104 independent reflections of which 190 were less than $2{\cdot}33\sigma(I)$. The structure was solved by direct methods and refined by a full-matrix least-squares procedure to the final residual $R=0{\cdot}065$. All hydrogen atoms were located and were refined isotropically. There is an intramolecular hydrogen bond between the 1-amino group and the 3-carboxyl group and the crystal packing is dominated by hydrogen-bond formation. The conformation of the cyclopentane ring is intermediate between that of an envelope and of a half-chair.

Introduction

It has been shown that 1-amino-1,3-dicarboxycyclopentane, an analogue of glutamate, is a substrate for glutamine synthetase (Stephani, Rowe, Gass & Meister, 1972). The enzyme interacts with one isomer of the racemic *cis* form of the analogue, but not with the *trans* form. A crystallographic study of the *trans* analogue has been undertaken as part of a study of the conformations of both isomers.

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Experimental

A mixture of the *cis* and *trans* isomers was separated by the procedure of Stephani, Rowe, Gass & Meister (1972). The crystal data are given in Table 1. Since the crystals, which grew as colorless needles in glacial acetic acid, formed in a noncentrosymmetric space group, it appears that the racemic mixture was resolved into its optical isomers on crystallization. Three-dimensional data were collected on a Syntex automated diffractometer equipped with a graphite monochromator and Cu $K\alpha$ radiation using the θ–2θ scan tech-