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The Crystal Structure of Tetramethylammonium Perchlorate

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The structure reported for tetramethylammonium perchlorate by Herrmann & Ilge (1929) is incorrect.

Crystals of tetramethylammonium perchlorate are tetragonal with $a = 8{\cdot}343 \pm 0{\cdot}002$ and $c = 5{\cdot}982 \pm 0{\cdot}003$ Å. The space group is $P4/nmm$ with $Z = 2$. The $(CH_3)_4N^+$ ions are in positions 2(*a*) with $\bar{4}2m$ symmetry and the ClO_4^- ions are in the positions 2(*c*), the required $4mm$ symmetry of the latter positions being achieved through a fourfold disorder of the perchlorate ions. The $(CH_3)_4N^+$ ion conforms very closely to the symmetry of a regular tetrahedron with $C\text{–}N = 1{\cdot}470 \pm 0{\cdot}014$ Å and C–N–C angles of $109{\cdot}4 \pm 0{\cdot}7°$ and $109{\cdot}5 \pm 0{\cdot}7°$. Because of the disorder, the observed dimensions of the perchlorate ion have rather large standard deviations, but within the significance of the present determination, the perchlorate ion is a regular tetrahedron with $Cl\text{–}O = 1{\cdot}50 \pm 0{\cdot}05$ Å.

Introduction

During the study of the structure of trimethyloxosulfonium perchlorate, $(CH_3)_3SO^+ClO_4^-$ (Coulter, Gantzel & McCullough, 1963) it became of interest to compare the observed structure with those of similar compounds. One compound considered in this connection was tetramethylammonium perchlorate, the structure of which has been reported by Herrmann & Ilge (1929). These authors proposed an ordered structure based on $P4/nmm$ in which the tetramethylammonium ions were placed in the positions 2(*a*) at 0, 0, 0 and $\frac{1}{2}, \frac{1}{2}, 0$ and the perchlorate ions in 2(*b*) at $0, 0, \frac{1}{2}$ and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, both with $\bar{4}2m$. This requires the large cations and anions to alternate with each other along the *c* axis of the unit separated by only 2·99 Å (center to center) and with a distance of 5·9 Å between column centers. Although this is the solution which results from the rigorous application of the ideal symmetry requirements of the space group, it is unacceptable on structural grounds. The present study was undertaken in order to resolve this discrepancy.

Experimental

Tetramethylammonium perchlorate was prepared by mixing aqueous solutions of tetramethylammonium chloride and silver perchlorate in the stoichiometric ratio. The filtered solution was concentrated by evaporation until about half of the theoretical yield of tetramethylammonium perchlorate was obtained. This material was then recrystallized from water. Crystals for the X-ray study were obtained by the slow evaporation of aqueous solutions and the selected specimens were prisms elongated on *c*.

The length of the *a* axis was obtained by means of an *hk*0 Weissenberg photograph upon which the *hk*0 reflections of a small quartz crystal were superimposed (Pabst, 1957). The axial ratio was determined by use of carefully aligned precession photographs of the (*h*0*l*) and (*hhl*) nets prepared with unfiltered Mo radiation. The resulting lattice parameters, based on $a = 4{\cdot}913$ Å for quartz are:

$$a = 8{\cdot}343 \text{ Å } (\sigma = 0{\cdot}002 \text{ Å}),\quad c = 5{\cdot}982 \text{ Å } (\sigma = 0{\cdot}003 \text{ Å}).$$

Herrmann & Ilge reported $a = 8{\cdot}27$, $c = 5{\cdot}97$ Å on the basis of X-ray diffraction measurements and $a = 8{\cdot}290$, $c = 6{\cdot}006$ Å on the basis of literature values of the density (1·379 g.cm^{-3}) and the goniometric axial ratio ($c:a = 0{\cdot}7246$). In some 230 observed unique reflections the only systematic extinctions were those for *hk*0 with $h + k = 2n + 1$, hence the space group is probably $P4/nmm$ as reported by Herrmann & Ilge. The observed density is 1·38 g.cm^{-3}, while that calculated for $Z = 2$ is 1·384 g.cm^{-3}.

The intensity data were taken from multiple-film Weissenberg photographs of the zero through fifth levels prepared with Cu $K\alpha$ radiation about the *c* axis. For interlayer scaling, and for use in the preliminary study, series of timed exposures of the (*h*0*l*) and (*hhl*) nets were prepared on the precession camera by use of Mo $K\alpha$ radiation. The crystal used for the intensity data was $0{\cdot}15 \times 0{\cdot}15 \times 1{\cdot}2$ mm. Since the value of μR for Cu $K\alpha$ radiation was only 0·3, no corrections for absorption in the specimen were made.

Determination of the structure

As a trial structure, the Me_4N^+ ions were placed in 2(*a*) with $\bar{4}2m$ symmetry and the ClO_4^- ions were placed in 2(*c*) with the assumption that the required $4mm$ symmetry of the latter positions is satisfied through disorder. Two-dimensional Patterson and Fourier summations on (110) confirmed that this trial structure is essentially correct with $z = 0{\cdot}410$ for

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chlorine. Nitrogen, carbon and chlorine atoms were clearly resolved in the Fourier summation but the oxygen positions were undetermined. Two disordered models were tried. One placed the tetrahedral perchlorate ions in two positions 90° apart with their $\bar{4}$ axes along the fourfold axis of the space group. In the other, the perchlorate ion was given full spherical disorder. Neither model was satisfactory. This suggested that the actual disorder is of some intermediate degree which has *4mm* but not full spherical symmetry.

A three-dimensional Patterson synthesis gave further evidence of the essential correctness of the assumed trial structure, as did a three-dimensional Fourier synthesis phased on the positions of Cl, N and C. A difference Fourier synthesis from which Cl, N and C were subtracted showed maxima about the chlorine position which suggested the following oxygen parameters involving fourfold disorder:

	x	y	z
O(1)	0·29	0·29	0·64
O(2)	0·13	0·13	0·42
O(3)	0·19	0·38	0·31

With appropriate weighting factors, these parameters were refined along with those of Cl, N and C by a full-matrix least-squares routine. In the first three cycles, chlorine was assigned anisotropic temperature factors and all other atoms were given isotropic factors. During these cycles the x (and y) parameters of O(1) behaved anomalously. This was probably due to the fact that this atom is close to the fourfold axis and is not resolved from its symmetry related atoms in the three-dimensional Fourier summations. Accordingly the x and y parameters for O(1) were assigned fixed values of 0·280 for the remainder of the least-squares refinement. After three more cycles of least-squares refinement, a three-dimensional Fourier difference synthesis was computed. This showed maxima which suggested hydrogen atoms in positions involving twofold disorder. Three final cycles of least-squares refinement were then computed which included the hydrogen atoms in the fixed positions shown in Table 1 with fixed isotropic temperature factors of 5·0 Å^2. Also the temperature factors on nitrogen and carbon were permitted to become anisotropic. The resulting positional parameters and their e.s.d. values are given in Table 1 while the temperature parameters and e.s.d. values are given in Table 2. A series of structure factors were then calculated in which only the parameter $x=y$ for O(1) was varied in steps of 0·005. The lowest value of R was obtained at $x=y=0{\cdot}280$. However, as expected, the R value was not very sensitive to this parameter and there is undoubtedly considerable dependence on the value of B used for O(1). In Table 3 the final structure factors calculated on the basis of the parameters in Tables 1 and 2 are compared with the observed values. The atomic scattering factors used in these calculations were those for neutral atoms in *International Tables for X-ray Crystallography* (1962). The factors designated 'C (valence),' which are due to McWeeny (1954), were used for carbon.

Table 1. *Final positional parameters**

(*a*) Heavier atoms (From least-squares refinement)

		Parameter	e.s.d.	Ratio of last shift to e.s.d.
N	x	0·7500		
	y	0·2500		
	z	0·0000		
C	x	0·7500		
	y	0·1062	0·0014	0·006
	z	0·1419	0·0021	0·023
Cl	x	0·2500		
	y	0·2500		
	z	0·4180	0·0008	0·005
O(1)	x	0·2800	0·0100	
	y	0·2800	0·0100	
	z	0·6405	0·0039	0·037
O(2)	x	0·1180	0·0027	0·052
	y	0·1180	0·0027	0·052
	z	0·4023	0·0055	0·130
O(3)	x	0·1682	0·0052	0·015
	y	0·3898	0·0046	0·078
	z	0·2954	0·0067	0·240

(*b*) Hydrogen atoms (Assigned positions)

	x	y	z
H(1)	0·650	0·075	0·172
H(2)	0·700	0·125	0·274
H(3)	0·700	0·025	0·070

Table 2. *Final temperature parameters from least-squares refinement*

(*a*) Atoms with anisotropic temperature parameters.
(The B's given here are related to the b's in the anisotropic temperature factor expression by the equations: $B_{11}=4a^2b_{11}$, $B_{33}=4c^2b_{33}$, *etc.*)

		Parameter	e.s.d.	Ratio of last shift to e.s.d.
N	B_{11}	3·5	0·4	0·015
	B_{22}	3·5	0·4	0·015
	B_{33}	5·3	0·7	0·019
C	B_{11}	5·2	0·5	0·020
	B_{22}	4·5	0·5	0·007
	B_{33}	7·3	0·7	0·007
Cl	B_{11}	3·2	0·1	0·016
	B_{22}	3·2	0·1	0·016
	B_{33}	5·6	0·3	0·014

(*b*) Atoms with isotropic temperature parameters

	B	e.s.d.	Ratio of last shift to e.s.d.
O(1)	7·0	0·7	0·014
O(2)	4·9	0·6	0·100
O(3)	5·0	0·9	0·057

A final three-dimensional Fourier difference synthesis showed no significant maxima or minima. The

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* The parameters given here are based on a cell with the origin at a center of symmetry. Because of disorder, oxygen atoms are given a statistical weight of ¼ and hydrogen atoms a weight of ½.

Table 3. *Observed and calculated structure factors*

K=0, L=0		
2	632	-664
4	163	167
6	275	-232
8	163	143
10	42	-45
K=1, L=0		
1	214	-133
3	218	186
5	62	-52
7	42	33
9	40	-38
K=2, L=0		
2	300	304
4	140	-158
6	194	172
8	102	-97
10	28	34
K=3, L=0		
3	337	-357
5	161	176
7	48	-48
9	42	49
K=4, L=0		
4	162	145
6	115	-109
8	56	58
K=5, L=0		
5	84	-98
7	23	22
9	36	-33
K=6, L=0		
6	100	99
K=7, L=0		
7	12*	-10
K=0, L=1		
0	89	-58
1	205	-114
2	115	122
3	228	-242
4	23	-36
5	48	43
6	35	31
7	71	58
8	38	-33
9	16*	-14
10	17	23
K=1, L=1		
1	632	647
2	222	182
3	182	-217
4	111	-91
5	194	171
6	38	39
7	158	-141
8	38	-38
9	64	62
10	29	31
K=2, L=1		
2	215	-218
3	40	27
4	131	149
5	47	46
6	64	-53
7	76	-71
8	37	34
9	18	24
10	22	-31
K=3, L=1		
3	135	163
4	70	82
5	142	-128
6	18*	-9
7	91	81
8	18*	6
9	35	-40
10	16	-19
K=4, L=1		
4	160	-161
5	73	-81
6	49	54
7	49	58
8	23	-29
9	18	-24
K=5, L=1		
5	119	99
6	18*	16
7	71	-70
8	14*	-11
9	34	37
K=6, L=1		
6	18*	-22
7	27	-23
8	12*	18
K=7, L=1		
7	61	63
K=0, L=2		
0	52	47
1	232	259
2	92	-122
3	198	-184
4	165	140
5	106	90
6	85	-68
7	82	-75
8	39	43
9	56	59
10	22	-27
K=1, L=2		
1	41	-42
2	22	12
3	48	17
4	78	-51
5	16*	28
6	98	-76
7	29	29
8	54	59
9	14*	-14
10	10*	-15
K=2, L=2		
2	107	149
3	116	130
4	137	-129
5	84	-74
6	74	59
7	37	31
8	35	-39
9	32	-39
10	22	28
K=3, L=2		
3	12*	-8
4	111	-111
5	16*	6
6	123	105
7	18*	-9
8	59	-61
9	12*	8
K=4, L=2		
4	114	94
5	72	64
6	59	-49
7	18*	-6
8	37	32
9	22	24
K=5, L=2		
5	18*	-12
6	61	-65
7	16*	17
8	39	40
K=6, L=2		
6	40	41
7	29	31
8	22	-27
K=0, L=3		
0	28	34
1	99	-105
2	47	-51
3	29	29
4	43	19
5	74	-60
6	16*	17
7	69	70
8	16*	-5
9	19	-35
K=1, L=3		
1	74	-101
2	111	124
3	59	-54
4	98	-98
5	13	17
6	84	73
7	34	16
8	59	-52
9	12*	8
K=2, L=3		
2	74	88
3	87	-91
4	82	-73
5	106	79
6	25	14
7	73	-59
8	13	-8
9	24	34
K=3, L=3		
3	91	72
4	98	95
5	33	-33
6	47	-38
7	16*	10
8	31	26
9	19	-18
K=4, L=3		
4	91	85
5	86	-75
6	36	-22
7	56	48
8	15	9
K=5, L=3		
5	14	18
6	45	42
7	14*	-5
8	28	-28
K=6, L=3		
6	14*	-6
7	33	-41
K=0, L=4		
0	92	-132
1	66	76
2	47	55
3	55	-50
4	21	-15
5	52	51
6	50	43
7	52	-44
8	25	-26
9	19	21
K=1, L=4		
1	57	68
2	74	-87
3	66	-81
4	80	82
5	47	42
6	55	-47
7	22	-18
8	28	33
9	19	18
K=2, L=4		
2	18	-20
3	68	68
4	14*	2
5	52	-53
6	34	-18
7	46	39
8	12*	9
K=3, L=4		
3	103	116
4	74	-64
5	68	-64
6	36	26
7	28	21
8	16	-18
K=4, L=4		
4	16*	3
5	50	46
6	14*	5
7	40	-32
K=5, L=4		
5	40	39
6	27	-28
K=6, L=4		
6	16	-18
K=0, L=5		
0	55	64
1	35	-56
2	56	-60
3	61	65
4	45	50
5	45	-37
6	46	-40
7	12	16
8	25	28
K=1, L=5		
1	35	-44
2	24	26
3	21	29
4	12	-7
5	33	-26
6	27	21
7	22	23
8	14	-13
K=2, L=5		
2	63	70
3	45	-44
4	56	-60
5	24	23
6	38	34
7	10*	-7
K=3, L=5		
3	24	-31
4	31	26
5	24	20
6	35	-30
7	10*	-9
K=4, L=5		
4	49	53
5	36	-14
6	24	-27
7	6*	2
K=5, L=5		
5	29	-17
6	20	18

The data are separated into groups having common values of k and l. The three columns in each group list values of h, $10F_o$, and $10F_c$, in that order. Unobserved reflections are indicated by * and the values of $10F_o$ given correspond to the minimum observable intensities

final value of R is 13·4% for all observed reflections and 12·7% if 110 and 101 are omitted.

Computing procedures

The Patterson, Fourier and difference syntheses involved in this study were computed by use of an unpublished routine written for the IBM 7090 by P. K. Gantzel & Håkon Hope in these laboratories. In its present form, the routine is applicable only to the calculation of structure factors and three-dimensional Fourier syntheses for centrosymmetric structures. The coefficients for the Fourier synthesis can be F_o, F_c or the difference between F_o and the contributions of any or all atoms present. The phases used are those calculated in the structure factor part which provides for either isotropic or anisotropic temperature factors. The contribution and phase of each atom is printed out for each reflection.

The least-squares refinement was carried out by use of ACA Computer Program No. 317 (UCLALS–1) written by P. K. Gantzel, R. A. Sparks & K. N. Trueblood for the IBM 7090. This program minimizes the weighted sum of the squares of the quantity $(KF_o - G|F_c|)$ by a full-matrix routine where K and G are scale factors. The program provides for several weighting options and for either isotropic or anisotropic temperature factors on the individual atoms. The anisotropic temperature factors are of the form:

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

The weighting scheme used was that of Hughes (1941) and unobserved reflections were omitted.

The standard deviations of the positional and temperature parameters were estimated from the inverse matrix of the normal equations. The shifts in parameters indicated in the last cycles of the least-squares refinements are given in Tables 1 and 2 as fractions of their respective e.s.d. values.

Discussion of the structure

A projection of the structure of tetramethylammonium perchlorate on (001) is shown in Fig. 1 and the observed bond distances and angles are given in Table 4. Within the significance of the observed positional parameters, both the tetramethylammonium ion and the perchlorate ion are regular tetrahedra. However, the observed distances and angles within the perchlorate ion are much less reliable than those in the tetramethylammonium ion because of the disorder which reduces the effective scattering factors for oxygen to one-fourth of the usual values. In spite of

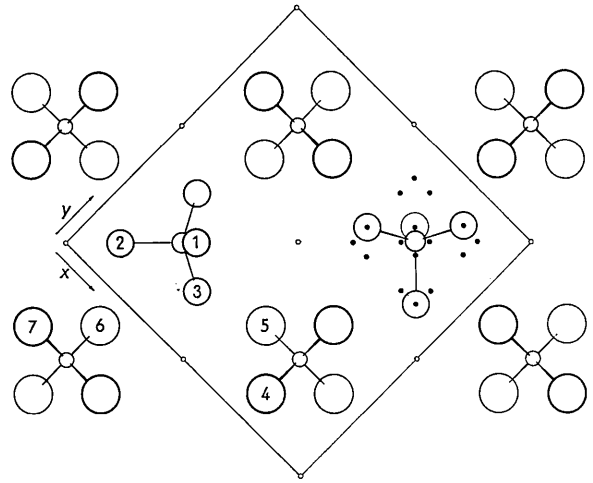

Fig. 1. Projection of the structure of $(CH_3)_4N^+ClO_4^-$ on (001). The circles represent, in order of decreasing size: CH_3, O, Cl and N. The black dots indicate alternate positions of oxygen atoms permitted by the disorder. The origin has been placed at a center of symmetry.

this limitation, the oxygen positions are sufficiently well defined to give a good representation of the nature of the disorder.

Table 4. *Bond distances and bond angles in* $(CH_3)_4N^+ClO_4^-$

(*a*) Distances

Bond	Distance	e.s.d.
C–N	1·470 Å	0·014 Å
Cl–O(1)	1·39	0·06
Cl–O(2)	1·56	0·04
Cl–O(3)	1·54	0·05

(*b*) Angles

(C–N–C)1	109·4 ± 0·7°
(C–N–C)2	109·5 ± 0·7
O(1)–Cl–O(2)	108·8 ± 3·5
O(1)–Cl–O(3)	113·7 ± 3·5
O(2)–Cl–O(3)	101·2 ± 2·5
O(3)–Cl–O(3′)	116·5 ± 2·5

The interionic packing involves only CH_3–O contacts if one defines a contact as a separation of less than $(R_A+R_B+0{\cdot}2)$ Å, where R_A and R_B are the van der Waals radii of the groups or atoms involved. The observed CH_3–O contacts, thus defined, are listed in Table 5 and may be compared with the sum of the van der Waals radii: $R_{CH_3}+R_O=3{\cdot}40$ Å. Some of the observed contacts are somewhat less than 3·40 Å. This may be due to a movement of the hydrogen atoms out of the line of the C–O contact through rotation about the C–N bond. The apparent disordering of the hydrogen atoms increases the likelihood of this possibility. The shortest CH_3–CH_3 and O–O separations have the same value, 4·20 Å.

Table 5. *Packing distances in* $(CH_3)_4N^+ClO_4^-$

See Fig. 1 for numbering af atoms

Atoms	Atom numbers*	Distance	Number of contacts per oxygen atom
O(1)–C	1–5′	3·04 Å	2
O(2)–C	2–7	3·44	2
O(2)–C	2–6	3·48	2
O(3)–C	3–4	3·19	1
O(3)–C	3–5	3·25	1

* Atom 5′ is related to atoms 5 by the lattice translation, *c*.

The structure of tetramethylammonium perchlorate is quite similar to that of trimethyloxosulfonium perchlorate. Both are related to the CsCl-type structure with variations caused by deviations of the ion symmetries from that of a true sphere. When the unit cell of tetramethylammonium perchlorate is doubled to correspond to that of trimethyloxosulfonium perchlorate, the lattice parameters are nearly equal:

	a	*c*
$(CH)_4N^+ClO_4^-$	11·80 Å	5·98 Å
$(CH_3)_3SO^+ClO_4^-$	11·66	5·99

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