The Crystal Structure of Nitronium Perchlorate*

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Nitronium perchlorate, $NO_2^+ClO_4^-$, has been investigated by three-dimensional analysis. There are four formula units in a monoclinic unit cell,

$$a = 9\cdot16, \quad b = 7\cdot08, \quad c = 7\cdot30 \text{ Å}, \quad \beta = 112\cdot1°,$$

space group $C/2c$. An apparent anomaly in the electron density of one of the oxygen atoms was explained by the anisotropy of the thermal motion. After anisotropic refinement ($R = 0\cdot13$) the bond lengths are $Cl-O = 1\cdot464 \pm 0\cdot007$ Å and $N-O = 1\cdot10 \pm 0\cdot01$ Å in ions which are slightly distorted from the tetrahedral and linear forms respectively. The N–O distance was reported as $1\cdot15 \pm 0\cdot01$ Å in nitronium nitrate (Grison, Eriks & de Vries, 1950); this value is confirmed by a new refinement of the published data. Chlorine $3d$ orbitals are involved in a strong π-bonding system in the perchlorate ion.

An anomalous statistical distribution of $|F|^2$ is due to a heavy-atom effect.

Introduction

Nitronium perchlorate, $NO_2^+ClO_4^-$, can be prepared by reaction between perchloric acid and dinitrogen pentoxide (Goddard *et al.*, 1946, 1950) or by passing dry gaseous chlorine dioxide into a mixture of oxides of nitrogen (Gordon & Spinks, 1940). It is a colourless crystalline solid at room temperature and decomposes without melting at 135 °C.

The existence of the nitronium ion was deduced from kinetic and cryoscopic measurements (Gillespie *et al.*, 1946, 1950), and the Raman spectrum indicated that the ion was linear (Ingold, Millen & Poole, 1946, 1950). A preliminary report of the present X-ray investigation (Cox, Jeffrey & Truter, 1948) showed that nitronium perchlorate consists of linear nitronium ions and tetrahedral perchlorate ions arranged in a distorted rock-salt structure so that each ion is approximately octahedrally co-ordinated to ions of opposite charge. Subsequently further examples of linear nitronium ions were found in dinitrogen pentoxide, $NO_2^+NO_3^-$ (Grison, Eriks & de Vries, 1950) in the dipyrosulphates (Steeman & MacGillavry, 1954) and in the trisulphate (Eriks & MacGillavry, 1954), with N–O bond lengths of $1\cdot15 \pm 0\cdot01$, $1\cdot09$ and $1\cdot06$ Å respectively.

The full X-ray investigation described below was undertaken not only to solve the stereochemical problem but also to determine accurate values for the bond lengths in the ions. Initially the analysis proceeded in a straight-forward fashion, but at the end of a three-dimensional isotropic refinement the residual $R = \Sigma|(|F_o| - |F_c|)|/\Sigma|F_o|$ was no better than $0\cdot24$ and

the electron density at the centre of one of the oxygen atoms was much lower than at the others. Various explanations proved unavailing, and the difficulty was only overcome more recently when the techniques and facilities for anisotropic refinement became available.

Experimental

Several crystals were prepared and sealed into Lindemann-glass tubes by Dr D. R. Goddard, and one of them, an equant crystal $0\cdot3$ mm. in radius, proved suitable for investigation. All X-ray photographs were taken with Cu $K\alpha$ radiation. Oscillation and rotation photographs about a, b, c and [101] showed that the unit cell is monoclinic with the dimensions:

$$a = 9\cdot16 \pm 0\cdot03, \quad b = 7\cdot08 \pm 0\cdot02, \quad c = 7\cdot30 \pm 0\cdot01 \text{ Å},$$
$$\beta = 112\cdot1 \pm 0\cdot4°.$$

From the systematic absences the space group is either $C2/c$ or Cc. It was not possible to determine the density accurately because of the reactivity of the crystals but an approximate value of 2 g.cm.$^{-3}$ was obtained compared with $2\cdot2$ g.cm.$^{-3}$ calculated for four molecules of $NO_2^+ClO_4^-$ per unit cell. Thus the ions must lie on two-fold axes or centres of symmetry if the space group is $C2/c$ but no symmetry in the ions is required for Cc. The complete structure analysis shows that the space group is $C2/c$.

For intensity measurements, oscillation photographs were taken about the a, b, c, and [101] axes and 364 out of a possible 466 intensities were strong enough to be observed and about another 30 reflections were inaccessible. A multiple-film technique was used and the intensities were estimated visually with the aid of a calibration slip. For the $h0l$ reflections a Weissenberg photographs was also taken. After the intensities

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had been corrected for Lorentz and polarization effects and had been correlated, an absorption correction was applied as for a spherical crystal 0·3 mm. in radius and with an absorption coefficient of 73·38 cm.$^{-1}$. The square roots of the corrected intensities yielded a set of structure amplitudes on an arbitrary scale. In the preliminary work the scale factor was adjusted to make $\Sigma|F_o|=\Sigma|F_c|$ but in the three-dimensional refinement it was refined in conjunction with the vibrational parameters. For the 14 reflections with $\sin\theta<0·3$ an extinction correction was made in the final stages of refinement. The revised intensities were taken as $I_t=I_o\exp(\alpha I_o)$ where I_t is the true value, I_o the observed value and $\alpha=0·0000175$, an empirical co-efficient obtained from the slope of a plot of $\log_e(I_c/I_o)$ against I_o.

Structure determination and three - dimensional isotropic refinement

Patterson projections showed that if the chlorine atoms lay on the two-fold axes (as required for a tetrahedral perchlorate ion in the space group $C2/c$) the nitrogen atoms also lay on these axes so that the nitronium ion could be either angular or linear. The complete solution to the structure was found from a three-dimensional Patterson section $P(u0w)$, shown in Fig. 1, and a line $P(0v\frac{1}{2})$. These syntheses were consistent with a two-fold axis so that the space group is $C2/c$. The interpretations of the various peaks are marked in Fig. 1, O' and O" denoting the two crystallographically different oxygen atoms of the perchlorate group and O_N the oxygen atom of the nitronium ion. For a two-fold axis, vectors must occur, in this Patterson section at $v=0$, for the pairs of atoms related by the axis, viz. O'–O', O"–O" and O_N–O_N. Six other peaks also appear because the chlorine on the $(0, y, \frac{1}{4})$ axis and the nitronium ion on the $(\frac{1}{2}, y, \frac{1}{4})$ axis have approximately the same y co-ordinates, and because O' of the glide-reflected molecule on the $(\frac{1}{2}, y, \frac{3}{4})$ axis lies in approximately the same plane as the chlorine atom and nitronium ion just mentioned.
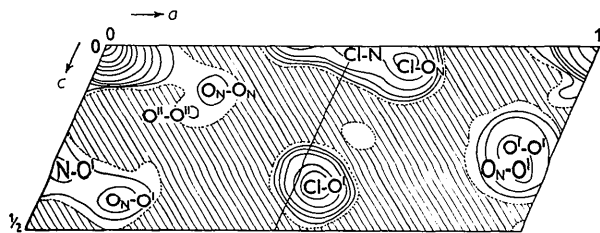
Fig. 1. Patterson section $v=0$. Negative areas are shaded and contours are at arbitrary intervals.

Figs. 2 and 3 show the structure as a whole. The co-ordinates obtained from the Patterson syntheses were refined by Fourier methods, using lines, bounded projections and sections. An isotropic temperature factor $\exp -B(\sin\theta/\lambda)^2$ with $B=1·2$ Å^2 was applied
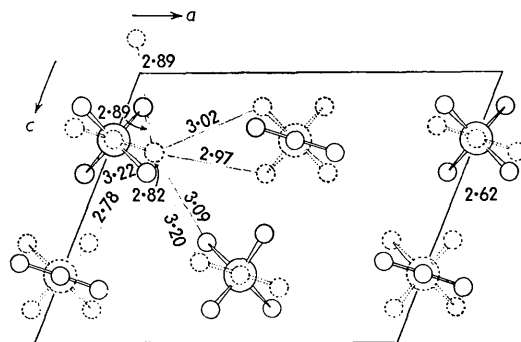
Fig. 2. Projection of the structure along [010]. Ions shown by full lines lie between the planes $y=0$ and $y=0·5$, those shown by broken lines lie between $y=0·5$ and $y=1·0$. The numbers are distances in Å to the neighbours indicated by the dotted lines.
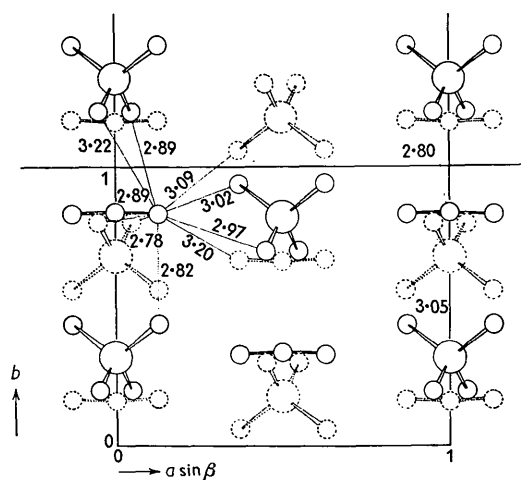
Fig. 3. Projection of the structure along [001]. Ions shown by full lines lie between the planes $z=0$ and $z=0·5$, those shown by broken lines lie between $z=0·5$ and $z=1·0$. The numbers are distances in Å to the neighbours indicated by the dotted lines.

at first, and later $B=1·6$ Å^2 was used for Cl and $B=3·2$ Å^2 for O and N. Further isotropic three-dimensional refinement was carried out on punched-card machines by differential syntheses with a back-shift correction for finite series errors and also by least squares; the two methods gave similar results. The residual R, for observed reflections only, was 0·24 and the co-ordinates corresponded to Cl–O distances of 1·42 and 1·42 Å and a N–O distance of 1·08 Å. The satisfactory agreement between the independent values for the Cl–O bond lengths was not matched by the agreement between the peak values for the electron density. While the difference between the observed and calculated peak densities for O' was only 0·1 e.Å^{-3} that for O" was 2·0 e.Å^{-3}. Since this latter difference was five times the estimated standard deviation of the electron density (Cruickshank, 1949), the discrepancy was too large to be ignored. At first, various

explanations were sought but without any success. For instance, when the Manchester University Ferranti Mark I electronic computer became available for refinement by differential syntheses (Ahmed & Cruickshank, 1953), further isotropic refinement was carried out with different temperature factors for the individual oxygens. Though the observed and calculated peak heights were made equal and the residual dropped slightly to 0·22, a large discrepancy of 0·08 Å appeared in the Cl–O bond lengths and the peak shapes were poor.

Three-dimensional anisotropic refinement

Another possible explanation for the anomaly, indicated by the statistical distribution of the intensities (see Appendix I), was that the space group was Cc, despite the evidence of the Patterson section, Fig. 1. Attempts to find a possible non-centrosymmetric structure by trial-and-error methods were unsuccessful. Since the elusive structure seemed likely to be pseudo-centrosymmetric, an attempt was made to find it in a systematic fashion by computing a difference Patterson synthesis with coefficients $(|F_o|^2 - |F_c|^2)$ where F_c was calculated from the final isotropic parameters. It was hoped that this synthesis would reveal that each of the peaks of the original F_0^2 synthesis was really double and hence how the pseudo-centrosymmetric structure was distorted from the assumed centrosymmetric structure. In fact, easily the most prominent feature of the difference Patterson synthesis was a large peak only 0·5 Å from the origin. Such a peak cannot arise from a difference in *interatomic vectors* and can only be due to a difference between the actual and assumed *atomic peak shapes*, most probably because of anisotropic thermal vibrations.

The space group $C2/c$ was therefore retained and three-dimensional anisotropic refinement on the Manchester Electronic computer was begun. (The false space-group indication of the statistical tests was later shown to be due to a 'heavy-atom' effect, see Appendix I). The vibrational parameters and the $|F_o|$ scale factor were refined by the differential synthesis methods described by Cruickshank (1956a), and after two cycles of refinement the residual R, excluding unobserved reflections, had fallen satisfactorily to 0·15. In these and later calculations the scattering factors of Berghuis et al. (1955) were used for Cl, O and N. The effect of the anisotropic motion was to restore the approximate equality of the two independent Cl–O bonds.

Subsequently the refinement was continued by the method of least squares on the Leeds University Ferranti Pegasus Computer. The function minimized was $R' = \Sigma w(|F_o| - |F_c|)^2$; w was at first taken as $1/|F_o|$ but later modified so that the average value of $w|\Delta F|^2$ was roughly constant for varying $|F_o|$. Unobserved planes were included with amplitudes $\frac{1}{2}|F_{min.}|$ where $|F_{min.}|$ was the minimum local observable value; for these a constant weight was required. The final weighting factor was $w = 1/(|F_o| + 0·02|F_0^2|)$ for observed planes and $w = \frac{1}{8}$ for the unobserved planes, the two groups then having the same average $w|\Delta F|^2$.

Ten cycles of refinement were carried out; for the last three cycles the observations for $\sin\theta < 0·3$ were corrected empirically for extinction in the manner described earlier. The refinement was stopped when the largest shift in any parameter was less than half the corresponding standard deviation and the average shifts were one fifth of the standard deviations. The final values for the atomic co-ordinates and their standard deviations are presented in Table 1. The final values for R were 0·141 for all planes and 0·126 for observed planes only; the observed and calculated structure factors are shown in Table 2.

The electron-density anomaly is no longer significant; for O'' the difference between the observed and calculated peak densities has fallen to 0·45 e.Å^{-3}.

Analysis of the anisotropic thermal motion

Before the molecular dimensions can be quoted an analysis of the vibrational motion is necessary so that the corrections to the bond lengths for rotational oscillations can be determined. The final values, referred to the monoclinic crystal axes, for the tensor components describing the anisotropic vibration of the atoms are given in Table 3, together with their standard deviations calculated in the least-squares refinement. The tensor components U_{ij} are those occurring in the temperature factor

$$\exp\left\{-2\pi^2(h^2a^{*2}U_{11} + 2hka^*b^*U_{12} + \ldots)\right\},$$

so that, for instance, U_{11} is the mean-square amplitude of vibration of the atom parallel to the a^* axis.

The main part of the atomic vibrations arises from the rigid-body vibrations of the molecules in the crystal, rather than from the internal vibrations of the molecules. For instance, using the data quoted by Herzberg (1945) for the vibrational analysis of the perchlorate ion, it can be shown that at room tem-

Table 1. *Atomic co-ordinates*

X, Y, and Z refer to orthogonal axes parallel to a, b, and c^*

	x/a	y/b	z/c	X	Y	Z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Cl	0·0000	0·3206	0·2500	−0·6874 Å	2·270 Å	1·692 Å	0·000 Å	0·002 Å	0·000 Å
N	0·0000	−0·1634	0·2500	−0·6874	−1·157	1·692	0·000	0·010	0·000
O'	0·0470	0·1989	0·1255	0·085	1·408	0·849	0·009	0·007	0·008
O''	0·1285	0·4395	0·3703	0·159	3·112	2·506	0·011	0·009	0·011
O$_N$	0·1269	−0·1698	0·2952	0·351	−1·202	1·997	0·009	0·008	0·008

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Table 2. *Observed and calculated structure factors*

For reflections too weak to be observed, F_O is given as half the minimum observable with a negative sign

h	F_o	F_e
h,0,0		
0	-	2680
2	1291	1153
4	- 16	7
6	254	261
8	194	209
10	61	50
h,0,2		
0	824	-1137
2	194	- 214
3	989	-1154
4	262	- 286
5	173	111
6	312	- 316
6	110	- 66
8	115	- 129
8	234	- 232
10	110	- 130
h,0,4		
0	117	86
2	- 18	20
3	455	491
4	158	152
5	374	419
6	144	138
6	180	177
8	233	243
10	167	200
h,0,6		
0	182	-190
2	92	- 82
3	368	-371
4	105	- 74
4	437	-443
8	296	-343
8	191	+222
10	134	-148
h,0,8		
0	139	136
2	228	227
4	174	204
6	156	139
8	105	120
h,1,0		
1	173	-134
3	84	73
5	- 19	- 26
7	63	- 52
9	47	- 30
h,1,1		
1	543	-478
1	337	-362
3	616	-637
3	304	-377
5	300	-318
5	173	-167
7	- 26	- 47
7	- 23	- 4
9	- 19	- 24
9	- 20	- 11
11	- 11	- 39
h,1,2		
1	188	-174
1	272	263
3	- 29	20
3	397	465
5	56	70
5	134	108
7	- 26	6
7	- 23	18
9	- 15	10
9	- 21	42
11	37	31
h,1,3		
1	- 23	23
1	385	-359
3	294	324
3	- 26	33
5	136	136
5	215	209
7	- 23	30
7	98	83
9	74	61
11	37	69
h,1,4		
1	83	- 66
1	60	49
3	164	-152
3	288	-286
5	- 21	- 34
5	260	-262
7	-16	10
7	-23	8
9	-21	14
11	69	- 31

h	F_o	F_o
h,1,5		
1	115	-113
1	114	60
3	100	-105
3	159	-135
5	- 17	- 15
5	215	209
7	98	83
9	74	61
h,1,6		
1	106	104
1	- 22	- 25
3	80	62
3	73	- 39
5	- 11	7
5	149	137
7	95	90
9	- 20	- 5
11	- 11	18
h,1,7		
1	118	145
1	147	153
3	57	57
3	152	149
5	239	246
7	206	213
9	59	72
h,1,8		
1	49	- 49
1	- 17	- 35
3	- 22	8
5	49	- 44
5	127	-106
9	61	- 59
h,2,0		
0	729	-738
2	540	-622
4	317	-324
6	152	-125
8	85	- 66
10	74	- 30
h,2,1		
0	814	936
2	89	- 36
2	606	719
4	81	- 32
4	49	42
6	199	208
6	220	227
8	109	120
8	225	238
10	78	74
h,2,2		
0	390	475
2	427	467
2	- 22	16
4	247	198
4	73	- 38
6	132	119
6	134	112
8	89	73
8	135	106
10	85	55
h,2,3		
0	422	-504
2	120	-107
2	935	914
4	145	-140
4	375	-426
6	135	-124
6	175	-129
8	43	- 46
8	203	-191
10	128	-112
h,2,4		
0	224	-212
2	59	- 40
2	155	-142
4	57	- 31
4	- 23	7
6	108	- 70
6	180	-150
8	206	-214
10	128	-111
h,2,5		
0	246	238
2	151	149
2	356	339
4	110	115
4	293	265
6	78	71
6	94	97
8	105	90
10	93	102

h	F_o	F_o
h,2,6		
0	167	136
2	- 20	16
3	282	300
4	- 32	29
4	253	228
6	150	133
6	160	151
10	101	109
h,2,7		
0	96	- 90
2	68	- 54
3	134	-135
3	143	-116
5	126	-110
5	154	-123
10	71	-107
h,2,8		
0	79	- 74
2	133	-149
3	134	-151
5	76	- 63
8	47	- 35
h,3,0		
1	383	-378
3	318	290
5	306	282
7	100	53
9	55	35
h,3,1		
1	240	256
1	146	-114
3	369	349
5	127	97
5	109	83
5	153	137
7	- 36	4
7	- 34	11
9	- 18	8
9	- 26	- 16
h,3,2		
1	132	-128
1	112	70
3	277	-293
3	376	-375
5	72	- 63
5	474	-494
7	- 32	16
7	208	-189
9	54	- 45
h,3,3		
1	155	-145
1	141	62
3	- 32	- 53
3	274	233
5	- 29	29
5	- 34	- 37
7	- 34	- 27
7	116	-106
9	- 27	- 21
h,3,4		
1	373	352
1	226	192
3	253	223
3	226	194
5	- 25	37
5	313	288
7	- 18	10
7	186	151
9	- 27	38
h,3,5		
1	- 30	- 13
1	124	90
3	- 22	- 13
3	104	60
5	- 15	17
5	- 30	31
7	134	113
9	120	78
h,3,6		
1	179	-163
1	116	-100
3	95	- 92
5	- 30	- 29
5	125	- 97
7	121	-112
9	88	- 67
h,3,7		
1	- 21	- 15
1	69	- 54
3	- 11	- 20
3	137	-118
7	98	- 69
7	- 26	- 17
9	- 20	- 28

h	F_o	F_e
h,3,8		
1	- 18	56
3	54	56
5	155	114
7	217	148
h,4,0		
0	195	-147
2	- 23	- 18
4	- 36	- 31
6	125	-110
8	74	- 49
h,4,1		
0	264	-269
2	246	-246
2	236	-262
4	131	-105
4	337	-339
6	108	-100
6	235	-282
8	100	-101
8	140	-166
10	62	- 74
h,4,2		
0	158	134
2	70	17
2	206	188
4	- 31	52
4	82	59
6	- 21	46
6	92	87
8	- 14	12
8	86	84
h,4,3		
0	531	607
2	231	256
2	436	495
4	101	60
4	300	287
6	107	86
6	278	286
8	157	198
h,4,4		
0	101	-117
2	69	- 68
2	154	-139
4	- 32	- 39
4	78	- 61
6	- 8	- 22
6	- 25	- 12
8	62	- 47
h,4,5		
0	273	-324
2	107	-122
2	322	-384
4	151	-121
4	81	- 54
8	138	-140
h,4,6		
0	54	52
2	73	62
4	-35	22
6	-20	7
8	56	30
h,4,7		
0	72	71
2	119	161
4	125	138
6	73	65
8	139	111
h,4,8		
0	- 9	- 6
2	-11	- 38
4	-18	-40
6	-11	-25
h,5,0		
1	97	73
3	190	-159
5	138	-127
7	66	- 54
9	- 14	- 44
h,5,1		
1	- 21	29
1	144	-140
3	226	239
3	181	143
5	114	77
5	175	191
7	- 22	- 16
7	- 72	21
9	- 14	- 4

h	F_o	F_e
h,5,2		
1	165	142
1	149	127
3	97	84
3	291	268
5	67	26
5	268	305
7	- 21	23
7	108	125
9	- 16	- 38
h,5,3		
1	171	-159
1	- 29	- 24
3	121	-112
3	- 30	14
5	- 29	4
5	162	-135
7	- 11	- 1
7	88	- 84
9	- 16	- 10
h,5,4		
1	160	-183
1	218	-232
3	95	-111
3	199	-192
5	167	-168
5	122	-103
9	- 15	- 23
h,5,5		
1	103	95
1	92	79
3	-15	32
3	-30	23
5	70	60
5	108	84
9	- 14	47
h,5,6		
1	74	77
1	58	60
3	73	64
3	80	56
7	81	63
h,5,7		
1	57	-54
1	134	-58
3	78	-65
7	73	-63
h,6,0		
0	288	327
2	283	288
4	169	177
6	146	108
8	84	82
h,6,1		
0	96	78
2	- 23	- 27
2	140	123
4	- 31	- 43
4	103	73
6	- 19	24
6	59	49
8	57	62
h,6,2		
0	286	-310
2	181	-210
2	222	-205
4	97	- 91
4	147	-142
6	89	- 96
6	121	-134
8	90	- 94
h,6,3		
0	148	-130
2	37	- 32
2	206	-222
4	- 26	- 22
4	177	-172
6	- 14	- 24
6	82	- 59
8	- 16	- 21
h,6,4		
0	154	203
2	52	62
2	218	224
4	116	113
4	158	126
h,6,5		
0	85	69
2	60	69
2	73	75
4	76	67
6	-17	-25

h	F_o	F_o
h,6,6		
0	82	- 94
2	134	-194
3	163	-163
4	108	-104
h,7,0		
1	- 24	17
3	77	- 55
5	- 25	10
h,7,1		
1	175	-165
1	140	-146
3	135	-153
3	145	-155
5	83	- 90
5	99	- 93
7	- 11	- 32
h,7,2		
1	- 25	28
1	100	-100
3	64	35
3	83	- 91
5	- 22	- 25
5	88	- 23
7	66	- 37
h,7,3		
1	104	73
1	70	67
3	71	85
3	104	99
5	128	113
7	- 11	59
h,7,4		
1	- 16	25
1	54	49
3	- 11	41
3	94	80
5	- 16	22
7	- 8	- 16
h,7,5		
1	49	- 52
1	108	-106
3	113	-143
h,7,6		
3	- 8	15
h,8,0		
0	241	-245
2	175	-169
4	103	- 78
h,8,1		
0	161	140
2	95	104
2	105	99
4	48	43
4	49	46
h,8,2		
0	158	147
2	85	94
2	141	149
4	78	68
h,8,3		
0	74	- 78
2	- 11	- 28
2	88	- 73
4	51	- 42
h,8,4		
0	44	- 57
2	84	- 96

Table 3. Vibration parameters

Values of U_{ij} in Å² and their estimated standard deviations

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Cl	$0{\cdot}057 \pm 2$	$0{\cdot}027 \pm 1$	$0{\cdot}036 \pm 1$	0	0	$0{\cdot}030 \pm 2$
N	$0{\cdot}065 \pm 7$	$0{\cdot}025 \pm 5$	$0{\cdot}057 \pm 7$	0	0	$0{\cdot}027 \pm 6$
O′	$0{\cdot}092 \pm 5$	$0{\cdot}041 \pm 4$	$0{\cdot}056 \pm 4$	$0{\cdot}007 \pm 4$	$0{\cdot}000 \pm 3$	$0{\cdot}047 \pm 4$
O″	$0{\cdot}106 \pm 6$	$0{\cdot}061 \pm 6$	$0{\cdot}091 \pm 6$	$-0{\cdot}038 \pm 5$	$-0{\cdot}034 \pm 5$	$0{\cdot}059 \pm 5$
O_N	$0{\cdot}060 \pm 4$	$0{\cdot}067 \pm 5$	$0{\cdot}055 \pm 4$	$0{\cdot}013 \pm 4$	$0{\cdot}011 \pm 4$	$0{\cdot}025 \pm 3$

for rotation only:

O′	$0{\cdot}035$	$0{\cdot}015$	$0{\cdot}019$	$0{\cdot}007$	$0{\cdot}000$	$0{\cdot}017$
O″	$0{\cdot}049$	$0{\cdot}035$	$0{\cdot}055$	$-0{\cdot}038$	$-0{\cdot}034$	$0{\cdot}029$
O_N	$(-0{\cdot}004)$	$0{\cdot}042$	$(-0{\cdot}002)$	$0{\cdot}013$	$0{\cdot}011$	$(-0{\cdot}003)$

perature the internal vibrations of the ion make contributions to the oxygen U_{ij} tensors of about 0·001 Å² along the Cl–O bonds and about 0·004 Å² in each of the two directions at right angles. These are much smaller than the values listed in Table 3. Accordingly the observed vibrations can be effectively analysed in terms of the translational and rotational oscillations of rigid molecular ions. We cannot claim high accuracy for the absolute values of the vibrations because there will be some error in the absorption correction.

For the chlorine and nitrogen atoms at the mass centres of the two ions the vibrational motion is thus due solely to translations of the ions; subtraction of these translational motions from the observed values for the oxygen atoms gives the contributions arising from the angular oscillations of the ions (see Table 3). From the principal axes of the U_{ij} tensor for chlorine, the translation of the perchlorate ion was found to involve a maximum r.m.s. amplitude of 0·26 Å at 37·5° to the positive a axis and 74·6° to the positive c axis in the plane parallel to (010), a minimum of 0·12 Å at right angles to this and in the same plane, and a vibration of 0·16 Å parallel to b. The largest motion is in the same direction as had been indicated by the Patterson difference synthesis. For the nitronium ion the r.m.s. translational amplitudes are 0·28 Å at 42·5° to the positive a axis and 69·6° to the positive c axis in the plane parallel to (010), 0·20 Å at right angles to this and in the same plane and 0·16 Å parallel to b.

The rotation of the nitronium ion around the 2-fold axis parallel to b is apparently negligible, but the mean-square displacement of O_N caused by rotation of the ion about its other 2-fold axis (which lies in the plane parallel to (010)) is $0{\cdot}042 \pm 0{\cdot}007$ Å². This corresponds to a r.m.s. angular oscillation of $11{\cdot}3 \pm 1{\cdot}0°$. The values for the two axes are curiously unequal, so that there is some hint of a hidden systematic error. However, taking them as they stand, they imply a correction (Cruickshank, 1956b) in the N–O bond length of +0·021 Å ($\pm 0{\cdot}005$ Å).

For O′ the direction of maximum vibration is perpendicular to the Cl–O′ bond, and the corresponding r.m.s. angular oscillation is $8° \pm 1°$; there is also a second angular oscillation perpendicular to the bond

with r.m.s. amplitude 5°; the correction to the Cl–O′ bond length for rotational oscillation is $+0{\cdot}019 \pm 0{\cdot}003$ Å. The direction of minimum vibration of O′ is along the Cl–O′ bond and is equal to the vibration of Cl in the same direction within experimental error.

For O″ the results are less satisfactory because, after subtraction of the translational motion, the direction of maximum vibration is apparently at an angle of 68° to the Cl–O″ bond while the minimum is at 30° to the bond. If the maximum and intermediate amplitudes, which correspond to r.m.s. angular oscillations of 12° and 7° respectively, are treated as perpendicular to the bond the correction is +0·042 Å. Alternatively, if we take the mean-square amplitudes in the directions corresponding by the tetrahedral symmetry to those used for O′, the correction is $+0{\cdot}038 \pm 0{\cdot}003$ Å. It seems reasonable to take the correction to the Cl–O″ bond as +0·04 Å.

As a check on the consistency of the vibrational parameters, the mean-square displacements for O′ and O″ in directions corresponding to a rotation about an axis normal to the Cl–O′–O″ plane were found to be 0·039 Å² and 0·040 Å² respectively, which shows that both atoms yield the same amplitude for the angular oscillation about this common axis.

Dimensions

Table 4 shows the bond lengths of the ions before and after correction for rotational oscillation and their standard deviations (a) calculated from those of the co-ordinates (b) including the uncertainty in the bond-length correction. The bond angles, which are unaffected by correction for rotational oscillation, and

Table 4. Bond lengths and angles

	Uncorr. (Å)	Corr. (Å)	E.s.d. (a) (Å)	E.s.d. (b) (Å)	Weighted mean of Cl–O′ and Cl–O″ (corr.) (Å)
Cl–O′	1·432	1·451	0·008	0·009	$1{\cdot}464 \pm 0{\cdot}007$
Cl–O″	1·445	1·485	0·010	0·010	
N–O	1·084	1·104	0·009	0·010	

O′–Cl–O′	$106{\cdot}0 \pm 0{\cdot}6°$	O′–Cl–O″	$111{\cdot}5 \pm 0{\cdot}5°$
O′–Cl–O″	$108{\cdot}8 \pm 0{\cdot}7$	O″–Cl–O′	$109{\cdot}6 \pm 0{\cdot}5$
O_N–N–O_N	$175{\cdot}2 \pm 1{\cdot}4$		

their standard deviations are also shown in Table 4. All the interionic distances of less than 3·5 Å were calculated. The minimum distance is 2·62 Å from O' to the nitrogen atom along the c axis; this and the other distances of less than 3·25 Å are indicated on Figs. 2 and 3.

Discussion of the molecular dimensions

The 4·8° bend in the nitronium ion is statistically significant ($\Delta/\sigma = 3·7$) and seems to be example of the distortion of a bond angle in the electrostatic field of the surrounding ions; we have verified from the known bending-force constant that the likely electrostatic forces in the crystal are of the required order of magnitude. The same effect is also shown by the perchlorate ion in which the angles bisected by the b axis are less than 109° 28' presumably because of attraction by the nitronium ions.

The bond length of $1·104 \pm 0·010$ Å in the nitronium ion is distinctly shorter than the value of $1·154 \pm 0·01$ Å obtained in nitronium nitrate (Grison, Eriks & de Vries, 1950) at -60 °C. As Grison had not considered any anisotropic vibrational motion, we have carried out a least-squares refinement of his data. The details of this are described in Appendix II. The revised value of the nitronium ion bond length is 1·148 Å, which with a small rotational oscillation correction of about 0·005 Å, yields a final value of $1·153 \pm 0·008$ Å, this is the same as Grison's. The difference between the observations of 1·104 and 1·153 Å is significant ($\Delta/\sigma = 3·8$). We cannot suggest any satisfactory explanation. It seems unlikely that the bonds in the two crystals are actually very different, particularly as the NO_2^+ symmetrical stretching frequencies, 1396·2 and 1394 cm.$^{-1}$ (Millen, 1950), are almost the same. Probably unidentified systematic errors have affected both structures; the most likely weakness of the nitronium perchlorate analysis is an underestimation of the rotational oscillation correction. The weighted mean of the two values is 1·134 Å.

An alternative estimate of the NO length can be obtained from CO_2, with which NO_2^+ is isoelectronic. In the isoelectronic pair CO and NO^+ an increase in force constant from 19·0 to $24·9 \times 10^5$ dynes cm.$^{-1}$ is correlated with a decrease in bond length from 1·128 Å to 1·062 Å (Herzberg, 1950; Miescher, 1955). In CO_2 and NO_2^+ the stretching force constants are 15·5 and 17·4 (Herzberg, 1945; Gray & Yoffe, 1955), so that the known length of 1·160 in CO_2 suggests a length of about 1·14 Å in NO_2^+, which accords well with the mean of the two X-ray values. However isoelectronic comparisons of this kind can be in error by up to 0·02 Å. The lengths reported in two other nitronium compounds, $1·09 \pm 0·04$ Å in $NO_2^+HS_2O_7^-$ (Steeman & MacGillavry, 1954) and 1·05 and 1·06 Å with uncertain error in $(NO_2^+)_2S_3O_{10}^-$ (Eriks & MacGillavry, 1954), are insufficiently accurate to be relevant to the present discussion.

Table 5. Cl–O *bond lengths in perchlorates*

Compound	Cl–O (Å)	Method	Reference
$LiClO_4.3\ H_2O$	$1·46 \pm 0·02$	3D	Prosen (1955)
$LiClO_4$	$1·44 \pm 0·01$	3D	Prosen (1955)
$KClO_4$	$1·43 \pm 0·01$	3D	Prosen (1955)
	$1·46 \pm 0·05$	2D	Mani (1957)
H_3OClO_4	$1·42 \pm 0·01$	3D	Lee & Carpenter (1959)*
NH_4ClO_4	$1·46 \pm 0·03$	2D	Venkatesan (1957)
$AgClO_4.C_6H_6$	$1·44 \pm 0·01$ $1·51 \pm 0·01$	3D	Smith & Rundle (1958)

* *Note added in proof.*—After anisotropic refinement and correction for rotational oscillation the revised Cl–O bond length in H_3OClO_4 is $1·452 \pm 0·005$ Å (Truter 1960).

In the perchlorate ion the two independent values for the Cl–O bonds agree within experimental error; the weighted mean is $1·464 \pm 0·007$ Å. The bond lengths found in perchlorate ions by other recent determinations are shown in Table 5. Taken with our value, we suggest that the weight of evidence favours a Cl–O length of 1·46 Å. We note for instance that the unequal values of 1·44 and 1·51 Å given by Smith & Rundle (1958) after a three-dimensional isotropic refinement are practically the same as the values of 1·43 and 1·51 Å obtained in the present analysis at the corresponding stage. Similarly though the three analyses of Prosen (1955), reported by Gillespie et al. average 1·44 Å, it seems likely that this should be increased a little by a rotational correction. A Cl–O bond length of 1·46 Å is substantially shorter than 1·65 Å, which is the sum of the tetrahedral covalent single-bond radii (Wells, 1950), or 1·70 Å, which is the Cl–O distance in OCl_2 (Dunitz & Hedberg, 1950). The stretching force constant in the perchlorate ion, $8·24 \times 10^5$ dyne cm.$^{-1}$, is also greater than in OCl_2, $4·93 \times 10^5$ dyne cm.$^{-1}$ (Herzberg, 1945), so that the bonds in the perchlorate ion must have substantial double-bond character. This is confirmed by an approximate molecular-orbital treatment (Cruickshank, 1960). In addition to the four σ-bonds formed with the chlorine $(3s)(3p)^3$ tetrahedral hybrids, there are two strong π-bonding molecular orbitals, one of which uses the $3d_{z^2}$ orbital and $2p\pi$ orbitals on all the oxygens and the other $3d_{x^2-y^2}$ and $2p\pi'$ orbitals. The overlap integrals between the $3d$ orbitals and the oxygen $2p$ combinations are rather large, perhaps as high as 0·6. By comparison the overlap between the adjacent carbon $2p\pi$ orbitals in benzene is about 0·3. A consequence is that the π-bonds in the perchlorate should be even stronger than in benzene. This agrees with the fact that the difference in length between the perchlorate bond and the Cl–O single bond is larger than between the benzene bond and the C–C single bond.

Of the possible comparisons of ClO_4^- with other isoelectronic ions, we shall mention only the recent determination (Atoji & Rundle, 1958) of the S–O length in SO_4^- as $1·488 \pm 0·009$ Å, which is 0·024 Å longer than Cl–O. As both σ and π electrons are

involved in these bonds, it is difficult to give a precise theoretical estimate for this difference.

Discussion of the refinement

A comparison of our final results for the 466 possible reflexions with those for the 364 actually observed shows some interesting features. The values of R are 0·141 and 0·126. The average standard deviations in the co-ordinates are 0·008 Å and 0·010 Å, so that these vary roughly inversely with the number of observations. The co-ordinates given by the observed reflections differ from the final co-ordinates by less than the corresponding standard deviations; fortuitously these alternative co-ordinates give better agreement between the uncorrected values for the two Cl–O bond lengths, 1·437 ± 0·010 and 1·433 ± 0·012 Å.

APPENDIX I

Distribution of intensities

One of the possible explanations of the electron-density discrepancy discovered in the isotropic refinement was that the space group might be Cc. Accordingly the distribution method (Howells, Phillips & Rogers, 1950) was applied to the observed intensities and compared with the results for the squares of the structure factors calculated from a centrosymmetrical model with the same temperature factor for all the atoms. From the results, Fig. 4(a), it appeared that the observed intensities corresponded to an acentric distribution so that the space group was Cc.

As mentioned, attempts to solve the structure on the basis of the space group Cc were unsuccessful and the problem was eventually solved by consideration of the anisotropic thermal motion. At the end of the anisotropic refinement on the centrosymmetrical structure the distribution of the squares of the calculated structure factors was re-calculated and found to give results close to the observed ones, Fig. 4(a). This seemed to suggest that a centrosymmetrical but anisotropic structure could give an acentric distribution, but we are grateful to the referee of a projected note on this for suggesting that the true explanation might be that this was an example of the 'heavy atom' effect (Hargreaves, 1955).

From the examples quoted by Hargreaves for a bromine (Atomic no. 35) compound and an antimony (Atomic no. 51) compound it would seem unlikely that a chlorine (Atomic no. 17) compound would depart appreciably from the ideal curve towards the theoretical curve for one heavy atom only. However, the average temperature factor after anisotropic refinement was $B = 1·85$ Å^2 for chlorine and $B = 4·41$ Å^2 for the light atoms, so that at high values of $\sin \theta$ the chlorine dominates the structure factors to a much greater extent than the atomic number alone indicates. If the chlorine atom only were present in the structure the distribution for three-dimensional data would be
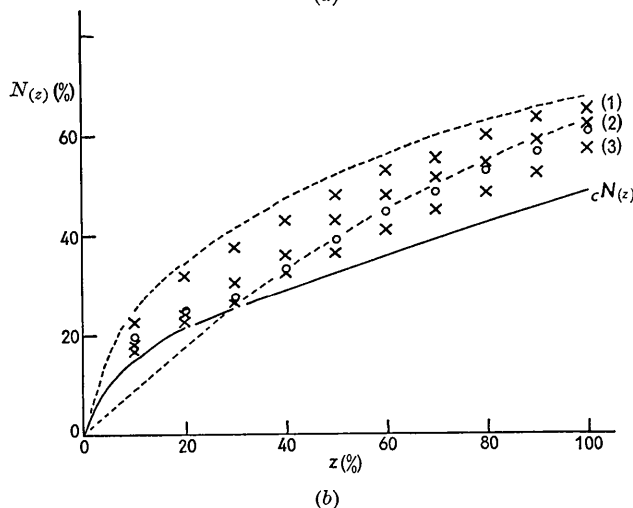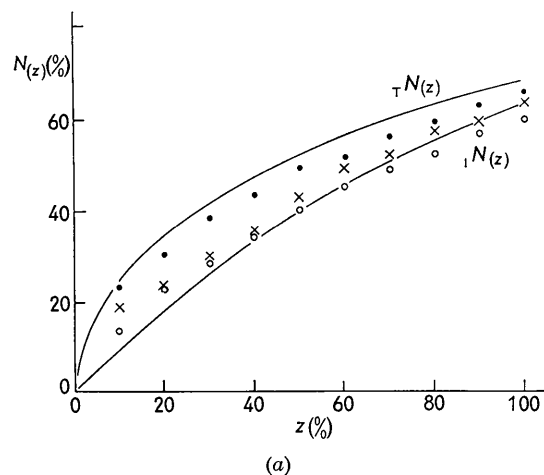

Fig. 4. (a) Statistical distribution of $F^2(hkl)$. Black circles—values calculated for a centrosymmetrical structure with the same isotropic temperature factor for all atoms. Crosses—values calculated from the final parameters, i.e. a centrosymmetrical structure with anisotropic thermal parameters for each atom. Open circles—observed intensities. (b) Statistical distribution of $F^2(hkl)$ excluding $F^2(h0l)$. Crosses—values calculated on assumptions (1), (2) and (3). Open circles—observed intensities.

determined by the geometrical structure factor for chlorine, which is unity for $h0l$ reflections and $\cos 2\pi ky$ or $-\sin 2\pi ky$ when l is even or odd respectively, thus the distribution of intensities, excluding $h0l$, would be $_cN(z)$ in Hargreaves' nomenclature. This hypothesis was tested by comparing the distributions, excluding the $(h0l)$ planes, for the squares of the structure factors calculated for the centrosymmetrical structure with the following $isotropic$ temperature factors:

(1) $B = 1·85$ Å^2 for all atoms.
(2) $B = 1·85$ Å^2 for Cl and 4·41 Å^2 for O and N.
(3) $B = 1·85$ Å^2 for Cl and $B = 7·00$ Å^2 for O and N.

The corresponding curves are shown in Fig. 4(b) together with the theoretical centric, acentric and $_cN(z)$ distributions.

It can be seen that (1) is reasonably close to the theoretical centric distribution so that, if all the atoms had had the same thermal motion, the presence of a chlorine atom would not have given misleading results. On the other hand (2), like the observed curve, might easily be mistaken for an acentric distribution. With distribution (3) the resemblance to the chlorine-only curve becomes marked.

APPENDIX II

A refinement of N_2O_5

The calculations were carried out by least squares on the Leeds University computer in the same fashion as the final refinement of nitronium perchlorate. The present refinement of Grison's data essentially confirms his results. Two cycles of isotropic and two cycles of anisotropic refinement were run with the 64 non-zero $|F_o|$ given by Grison (11 reflections observed as zero by him were verified to have only small F_c). The neutral-atom scattering factors of Berghuis *et al.* (1955) were used, and the weights were taken as

$$w = 1/\{2 + |F_o| + (1/16)|F_o|^2\},$$

where $|F_o|$ was twice the value listed by Grison, so as to refer to the whole cell. The final value of R for the 64 reflections was 0·114, as compared with Grison's 0·120 including the 11 zero F_o. During the refinement the scale of the observed structure factors was raised by 11%.

The apparent vibrational motion was very small, varying from $U_{33} = 0·013$ Å^2 for N_1 to $U_{11} = -0·004$ Å^2 for N_2; as the e.s.d.'s of these determinations are 0·008 and 0·004, the apparent motion is hardly different from zero. However the two types of oxygen atoms did seem to vibrate a little more than the nitrogen atoms at the centre of their ions, so the rotational corrections were included. With rotational corrections of 0·005 and 0·003 Å, the final values for the NO bonds are $1·153 \pm 0·008$ Å and $1·255 \pm 0·005$ Å in the NO$_2^+$ and NO$_3^-$ ions respectively. These are little different from Grison's values of 1·154 and 1·243 A. The e.s.d.'s were calculated from the standard least-squares formula with the number of independent parameters properly counted, but without any allowance for the uncertainty of the rotational correction.

We thank Dr R. Hine for his help with this refinement.

References

AHMED, F. R. & CRUICKSHANK, D. W. J. (1953). *Acta Cryst.* **6**, 765.

ATOJI, M. & RUNDLE, R. E. (1958). *J. Chem. Phys.* **29**, 1306.

BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A.L. (1955). *Acta Cryst.* **8**, 478.

COX, E. G., JEFFREY, G. A. & TRUTER, M. R. (1948). *Nature, Lond.* **162**, 259.

CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.

CRUICKSHANK, D. W. J. (1956a). *Acta Cryst.* **9**, 747.

CRUICKSHANK, D. W. J. (1956b). *Acta Cryst.* **9**, 757.

CRUICKSHANK, D. W. J. (1960). In preparation.

DUNITZ, J. D. & HEDBERG, K. (1950). *J. Amer. Chem. Soc.* **72**, 3108.

ERIKS, K. & MACGILLAVRY, C. H. (1954). *Acta Cryst.* **7**, 430.

GILLESPIE, R. B., SPARKS, R. A. & TRUEBLOOD, K. N. (1959). *Acta Cryst.* **12**, 867.

GILLESPIE, R. J., GRAHAM, J., HUGHES, E. D., INGOLD, C. K. & PEELING, E. R. A. (1946). *Nature, Lond.* **158**, 480.

GILLESPIE, R. J., GRAHAM, J., HUGHES, E. D., INGOLD, C. K. & PEELING, E. R. A. (1950). *J. Chem. Soc.* p.2504.

GODDARD, D. R., HUGHES, E. D. & INGOLD, C. K. (1946). *Nature, Lond.* **158**, 480.

GODDARD, D. R., HUGHES, E. D. & INGOLD, C. K. (1950). *J. Chem. Soc.* p. 2559.

GORDON, W. E. & SPINKS, J. (1940). *Canad. J. Res.* B, **18**, 358.

GRAY, P. & YOFFE, A. D. (1955). *Chem. Rev.* **55**, 1069.

GRISON, E., ERIKS, K. & VRIES, J. L. DE (1950). *Acta Cryst.* **3**, 290.

HARGREAVES, A. (1955). *Acta Cryst.* **8**, 12.

HERZBERG, G. (1945). *Molecular Spectra and Molecular Structure.* II. New York: Van Nostrand.

HERZBERG, G. (1950). *Molecular Spectra and Molecular Structure.* I. 2nd ed. New York: Van Nostrand.

HOWELLS, B. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210.

INGOLD, C. K., MILLEN, D. J. & POOLE, H. G. (1946). *Nature, Lond.* **158**, 481.

INGOLD, C. K., MILLEN, D. J. & POOLE, H. G. (1950). *J. Chem. Soc.* p. 2576.

LEE, F. S. & CARPENTER, G. B. (1959). *J. Phys. Chem.* **63**, 279.

MANI, N. V. (1957). *Proc. Indian Acad. Sci.* A, **56**, 143.

MIESCHER, E. (1955). *Canad. J. Phys.* **33**, 355.

MILLEN, D. J. (1950). *J. Chem. Soc.* p. 2606.

PROSEN, R. (1955). Ph.D. Thesis, University of California at Los Angeles.

SMITH, H. G. & RUNDLE, R. E. (1958). *J. Amer. Chem. Soc.* **80**, 5075.

STEEMAN, J. W. M. & MACGILLAVRY, C. H. (1954). *Acta Cryst.* **7**, 402.

WELLS, A. F. (1950). *Structural Inorganic Chemistry,* 2nd ed. Oxford: University Press.

VENKATESAN, K. (1957). *Proc. Indian Acad. Sci.* A, **56**, 134.