A detailed refinement of the crystal structure of hydroxonium perchlorate. By Mary R. Truter,

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The crystal structure of the monohydrate of perchloric acid, $HClO_4 \cdot H_2O$ was determined by Lee & Carpenter (1959), (hereafter referred to as LC) who confirmed the earlier theory that the substance is hydroxonium perchlorate, $H_3O^+ClO_4^-$. They obtained a mean value for the Cl–O bond length in a tetrahedral perchlorate ion of 1.42 ± 0.01 Å which is considerably less than 1.46 ± 0.01 Å reported (Truter, Cruickshank & Jeffrey, 1960) (TCJ) in a similar simple perchlorate, the nitronium salt, $NO_2^+ClO_4^-$. Both determinations were carried out three-dimensionally with observations made photographically at room temperature; they differed in the extent of refinement. For nitronium perchlorate the anisotropic thermal parameters for each atom were determined and the correction (Cruickshank, 1956) for the systematic error due to rotational oscillation was applied; this correction was 0.02 Å and 0.04 Å for the independent Cl–O bond lengths so that the uncorrected lengths were about the same as those of LC. For hydroxonium perchlorate only the individual isotropic thermal parameters for the atoms other than hydrogen were found and these were higher for the oxygen atoms than for the chlorine atom. It appeared likely that the discrepancy between the two sets of values for the Cl–O bond lengths might arise from omission of the correction for rotational oscillation. The present note describes the result of determining and applying this correction for hydroxonium perchlorate.

The structure found by LC consists of four hydroxonium ions (of which only the oxygen atoms could be found), each designated O_5, and four perchlorate ions in the unit cell with dimensions

$$a = 9.065, \quad b = 5.569, \quad c = 7.339 \text{ Å} .$$

The space group is *Pnma* and the Cl atoms and the oxygen atoms (designated O_1 and O_2) of the perchlorate ion all lie, like O_5, in the mirror planes; the remaining oxygen

atoms of the perchlorate ions O_3 and O_4 are related by the mirror planes.

For the three-dimensional anisotropic refinement the 201 non-zero $|F_o|$ listed by LC were used. The procedure followed was the same as that for nitronium perchlorate and the same scattering factors were used. Four cycles of least-squares refinement were carried out and the residual R was reduced to 0.057 (from 0.077 LC). The $|F_o|$ scale factor determined by the least-squares process was 1.006; the weighting scheme was $w = 1/|F_o|$. The final co-ordinates and their standard deviations are given in Table 1 and the vibration parameters and their standard deviations in Table 2. The values in Table 1(a) differ only slightly from those of LC (the largest change being 0.01 Å in z for O_5) but the thermal motion is markedly anisotropic. The motion of the perchlorate ion, assuming it to be a rigid body, was calculated with respect to the axes of inertia which were determined from the atomic masses and the dimensions given by the uncorrected co-ordinates in Table 1(a): they were I, normal to the O_1–Cl–O_2 plane (i.e. parallel to b); II, in a direction not quite the bisector of the O_1–Cl–O_2 angle but at $62°$ to O_1–Cl; and III, orthogonal to I and II. The mean square amplitudes of translation are 0.044 Å², 0.050 Å² and 0.056 Å² parallel to I, II and III respectively while the r.m.s. rotational oscillations are $8.3°$, $8.7°$ and $10.5°$ about I, II and III respectively. These large rotational oscillations give rise to an appreciable systematic error in the bond lengths; the correction are ± 0.026 Å for Cl–O_1, $+0.027$ Å for Cl–O_2 and 0.029 Å for Cl–O_3 and the corrected co-ordinates are given in Table 1(b). The dimensions of the perchlorate ion calculated from the corrected co-ordinates are given in Table 3.

The perchlorate ion does not differ significantly from a regular tetrahedron and the mean Cl–O length of 1.452 ± 0.005 Å is now in agreement with the value obtained for the nitronium salt (TCJ). This refinement has

Table 1. *Atomic co-ordinates in* Å

(a) before and (b) after correction for rotational oscillation, and their standard deviations

	$x(a)$	$\sigma(x)$	$x(b)$	$y(a)$	$\sigma(y)$	$y(b)$	$z(a)$	$\sigma(z)$	$z(b)$
Cl	3.8229	0.0029	(3.8229)	1.3923	0	(1.3923)	1.4440	0.0024	(1.4440)
O_1	2.7257	0.0094	2.7066	1.3923	0	(1.3923)	0.5314	0.0088	0.5142
O_2	5.0616	0.0083	5.0842	1.3923	0	(1.3923)	0.7647	0.0103	0.7505
O_4	3.7084	0.0077	3.7061	0.2319	0.0083	0.2081	2.2810	0.0065	2.2977
O_5	6.1075	0.0085	—	4.1769	0	— —	2.3875	0.0078	—

Table 2. *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	0.055 ± 1	0.043 ± 2	0.051 ± 1	0	0	0.000 ± 1
O_1	0.069 ± 5	0.087 ± 7	0.071 ± 5	0	0	-0.015 ± 5
O_2	0.061 ± 6	0.098 ± 8	0.087 ± 6	0	0	0.021 ± 5
O_3	0.110 ± 6	0.080 ± 6	0.072 ± 5	-0.006 ± 5	0.025 ± 4	0.008 ± 5
O_5	0.069 ± 5	0.051 ± 6	0.097 ± 5	0	0	0.004 ± 4

Table 3. *Bond lengths and angles*

Cl–O$_1$	1·453 ± 0·009 Å	weighted
Cl–O$_2$	1·439 ± 0·009	mean
Cl–O$_3$	1·465 ± 0·008	1·452 ± 0·005 Å

O$_1$–Cl O$_3$	108° 9′ ± 30′
O$_1$–Cl–O$_2$	111° 30′ ± 30′
O$_2$–Cl O$_3$	110° 30′ ± 30′

again demonstrated the importance of correcting for rotational oscillation.

Hydrogen atoms

Lee & Carpenter were unable to find the hydrogen atoms in projection, nor did they find three O$_5$ $\cdots$ O distances shorter than the others such as might be expected for a hydrogen-bonded H$_3$O$^+$ ion. They suggested either (i) that there is free rotation of the hydrogen atoms about the oxygen atom, or (ii) that the hydrogen atoms were equidistant from pairs of oxygen atoms on the neighbouring perchlorate ions.

In an endeavour to locate the hydrogen atoms a three-dimensional difference synthesis was carried out with F_c from the final anisotropic parameters. As might be expected from the small value of R, there were no large peaks or throughs and the positive values within a radius

of 1·5 Å from O$_5$ were smaller than those in positions which could not be attributed to hydrogen atoms. This evidence indicates the free rotation of the hydroxonium ions, and is consistent with the preliminary results of a neutron-diffraction study (Smith & Levy, 1959).

Computation was carried out on the Leeds University Ferranti Pegasus computer with programmes published in 1960 (Cruickshank, Pilling and in part Bujosa, Lovell & Truter).

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Coloured polyhedra. By G. S. PAWLEY, *Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England.*

Introduction

Klein (1884) gave an account of the subgroups contained in any point-group, but thought it unnecessary to enumerate these subgroups in his book. Recently Wittke & Garrido (1959) tabulated some of these, but restricted their attention to crystallographic point-groups. In this present note the treatment is extended to the icosahedral point-groups, and the general case for the point-groups $r, r2, rm, \bar{r}, \bar{r}m, r/m$ and r/mmm can be obtained by Klein's analysis. The notation here used is the same as that of Wittke & Garrido.

Definition of a coloured polyhedron

A 'coloured polyhedron' has its shape governed by a point-group G but has its faces coloured in a way that obeys a different point-group g. g is a subgroup of G, and g' is any group for which g.g' = G. G and g have M and m_g faces in their general forms respectively, thus the numner of colours s required for the general coloured polyhedron is M/m_g. All the symmetry operations of G not included in g do not necessarily form a group, but must change the colour of any face on which they act, and these are called colour symmetry operations.

Multicoloured faces

The number of different colours related by m_c (colour mirror), r_c (colour r-fold axis) and $r_c m_c$ (r_c in the plane of m_c) are clearly 2, r and $2r$ respectively. A special form of G is produced if the face normal lies in a mirror plane

or parallels an r-fold axis, and this is denoted in the tables by m or r. The faces of any special form can be sectioned by lines in such a way that the sections, considered as separate, obey the general point-group symmetry. These lines can be obtained from the edges

Table 1. *The number of colours n present on each face of the special forms of the point group* 5m3m

g	m_g	s	5	3	2	m	g′	*
5m3m	120	1	1	1	1	1	1	
532	60	2	2	2	2	2	m	
52	10	12	2,10	6	2,4	2	3m	
5	5	24	2,10	6	4	2	3m	
$\bar{5}$	10	12	2,10	6	4	2	3m	
5m	10	12	1,5	3	2	1,2	3	
5m(2)	20	6	1,5	3	2	1,2	3	
m3(2)	24	5	5	2,3	1,4	1,2	5	*
23	12	10	10	2,6	2,4	2	5m	*
32	6	20	10	2,6	2,4	2	5m	*
3	3	40	10	2,6	4	2	5m	*
$\bar{3}$	6	20	10	2,6	4	2	5m	*
3m	6	20	5	1,6	2,4	1,2	5	*
3m(2)	12	10	5	1,6	2,4	1,2	5	*
222	4	30	10	6	2,4	2	5m	*
2	2	60	10	6	2,4	2	5m3m	*
mmm(2)	8	15	5	3,6	1,4	1,2	5	*
mm(2)	4	30	5,10	3,6	1,2,4	1,2	532	*
2/m	4	30	5,10	3,6	2,4	1,2	532	*
m	2	60	5,10	3,6	2,4	1,2	532	*
$\bar{1}$	2	60	10	6	4	2	532	*
1	1	120	10	6	4	2	5m3m	*

* Denotes a crystallographic subgroup.