Crystal Structures of some Hydrated Compounds.

I. $LiClO_4 \cdot 3H_2O$, $LiI \cdot 3H_2O$, $Ba(ClO_4)_2 \cdot 3H_2O$.

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(With 1 figures.)

The observed existence of the tabulated hydrates as solid phases, which afford another example of the general similarity (long recognised by chemists) of lithium to metals of the second group, suggests a similarity in the structural functions of the complexes $Li_2 \cdot 6\,H_2O$ and $Mg \cdot 6\,H_2O$. It also suggests that the Li^+ ion is coordinated to either three or six water molecules in these crystals. An examination by X-ray methods of the crystal structures of some of these hydrates has therefore been undertaken. The present report will recount some observations on the structures of $LiClO_4 \cdot 3\,H_2O$, $LiI \cdot 3\,H_2O$, and also of $Ba(ClO_4)_2 \cdot 3\,H_2O$; following papers will deal with hydrates of the formula $Me(ClO_4)_2 \cdot 6\,H_2O$, where Me is Mg, Mn, Fe, Co, Ni, Zn and Cd, which form an interesting hitherto unstudied isomorphous series (except the Cd compound); and further with the structure type $MeX_2 \cdot 6\,H_2O$ (where Me is an alkaline earth, and X a halogen) previously described by Herrmann[1]).

Substance	MP	Substance	MP
$LiCl \cdot 3H_2O$	$-15°$	$MgCl_2 \cdot 6H_2O$	$118°$
$LiBr \cdot 3H_2O$	3	$MgBr_2 \cdot 6H_2O$	152—65
$LiI \cdot 3H_2O$	73	$MgI_2 \cdot 6H_2O$	> 190
$LiClO_3 \cdot 3H_2O$[2])	8	$Mg(ClO_3)_2 \cdot 6H_2O$	35—40
$LiClO_4 \cdot 3H_2O$	95	$Mg(ClO_4)_2 \cdot 6H_2O$	147
$LiMnO_4 \cdot 3H_2O$		$Mg(MnO_4)_2 \cdot 6H_2O$	
$LiNO_3 \cdot 3H_2O$	30	$Mg(NO_3)_2 \cdot 6H_2O$	90

Melting points are taken from International Critical Tables or from Mellor's Comprehensive Treatise, except as noted.

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1) Z. Herrmann, Z. anorg. allgem. Chem. **187**, 231. 1930; **196**, 79; **197,** 212, 339. 1931.

2) L. Berg, Z. anorg. allgem. Chem. **166**, 231. 1927; **181**, 131. 1929.

$LiClO_4 \cdot 3\,H_2O.$

According to Groth, $LiClO_4 \cdot 3\,H_2O$ crystallises in the hexagonal system in prisms $10\bar{1}0$ terminated by $10\bar{1}1$, with the axial ratio $c/a = .704$ and density 1.84. While the symmetry class is not assigned, neither of two observers remarked any departure from holohedral symmetry. A redetermination of the density by the suspension method gives $1.89 \pm .01$.

From Laue, oscillation, and powder photographs in *Mo* radiation the symmetry is D_{6h} and the lattice constants are:

Hexagonal, $a = 7.71$, $c = 5.42$, $c/a = .704$, $Z = 2$, density $= 1.90$.
Absent reflections $hh.l$ with l odd.

A reasonable structure has been developed in the space group C_{6v}^4 and has been tested by comparisons of calculated and observed intensities of reflections. The structure lacks a horizontal plane of symmetry.

The following arrangement in C_{6v}^4 was assumed.

a) $2\,Li$ in $00z$.
b) $2\,Cl$ in $\frac{1}{3}\frac{2}{3}0$; $2\,O_I$ in $\frac{1}{3}\frac{2}{3}w$.
c) $6\,O_{II}$ in $u\bar{u}v$; $6\,Aq$ in $u'\bar{u}'v'$.

The ClO_4^- ion was assumed to be a regular tetrahedron with the Cl—O distance 1.50; this requires that $w = 100°$, $u = 120 \pm 38°$, $v = -33°$, and leaves only u' and v' as variables if the lithium atoms are neglected.

The first step in the structure determination is to find values of u and u' that will give agreement between observed intensities and calculated structure amplitudes in the prism zone (reflections $hk.0$). The structure amplitudes are calculated from the following F-curves.

$\sin \theta/\lambda =$	0	.1	.2	.3	.4	.5
Li	2	1.9	1.8	1.6	1.3	1.1
Cl	10	9.9	9.4	8.7	7.8	6.8
O	10	8.0	5.5	3.8	2.7	2.1

Table I shows that satisfactory agreement is obtained with the values $u = 158°$, $u' = 45°$.

The second step is to match the intensities of general planes $(hk.l)$ by a suitable choice of v'. Table I shows that satisfactory agreement is obtained with the c-parameters $z = 90°$, $w = 100°$, $v = -33°$, $v' = 180°$. The structure is thus completely determined.

While the lithium atom contributes very little to the intensity of the diffracted beams, nevertheless its a-parameters may be regarded as

certain. This follows from the fact that in the hexahydrated divalent perchlorates, which have the same projection of the structure on the basal plane as $LiClO_4 \cdot 3\,H_2O$, the metal atoms can be located from intensity considerations on the axes corresponding to $00z$. The c-parameter is a guess.

With these values of the variables the following interatomic distances are calculated:

Li—6 Aq 2.14.

Aq—Aq 2.88, 3.18 octahedron edges.

O_{II}—O_{II} 3.16, O_{II}—O_I 3.10 in different tetrahedrons.
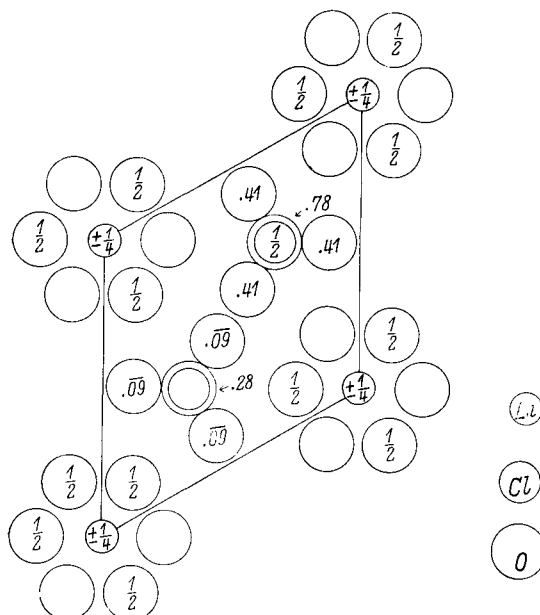
Aq—O_I 3.04, Aq—O_{II} 2.94, 3.28.

Fig. 1. Projection of the structure of $LiClO_4 \cdot 3\,H_2O$
on (001). $a = 7.71$, $c = 5.42$.

Atoms not numbered are at zero height, the heights
of the others are indicated as fractions of the c-axis.

This structure, represented in Figure 1, places 6 waters at the points of a flattened octahedron about each lithium atom. Successive octahedrons along the $(00z)$ axis share faces parallel to the basal plane.

Summary: The hexagonal unit of $LiClO_4 \cdot 3\,H_2O$ with $c = 5.42$, $a = 7.71$, $Z = 2$, has the atoms in the following positions of space group C_{6v}^4:

a) 2 Li in $00z$, $z = 90^c$.

b) 2 Cl in $\frac{1}{3}\frac{2}{3}0$; 2 O_I in $\frac{1}{3}\frac{2}{3}w$, $w = 100°$.

c) 6 O_{II} in $u\bar{u}v$, $u = 158°$, $v = -33°$.

   6 Aq in $u'\bar{u}'v'$, $u' = 45°$, $v' = 180°$.

Table I. Oscillation Photographs of $LiClO_4 \cdot 3H_2O$.

hk	sin θ/λ for hk·0	l = 0 F I	l = 1 |F| I	l = 2 |F| I	l = 3 |F| I	l = 4 |F| I
00			0 a	56 st	0 a	25 st
10	.075	— 12 m	30 vst	15 m	21 st	7 a
11	.130	38 st	0 a	5 w	0 a	17 st
20	.150	— 7 mw	48 vst	18 st	31 vst	18 mst
21	.198	— 31 st	24 st	19 st	10 mst	9 mst
30	.225	3 w	13 mw	10 m	24 mst	18 mst
22	.260	37 st	0 a	13 m	0 a	23 st
31	.270	7 w	16 st	11 m	19 st	14 mst
40	.300	— 23 m	13 m	18 mst	15 mst	7 w
32	.327	1 a	18 mst	8 a	14 mst	9 w
41	.342	24 st	9 m	5 m	5 w	17 st
50	.375	— 16 m	12 w	16 mst	3 w	7 m
33	.390	50 st	0 a	32 st	0 a	17 st
42	.396	— 7 w	16 m	6 w	13 mst	3 a
51	.417	— 4 w	18 st	9 m	17 st	13 mst
60	.450	7 m	6 a	5 mw		
43	.455	— 11 mst	11 mst	9 m		
52	.467	15 st	8 mw			
61	.490	— 11 mst	8 m			

$LiI \cdot 3H_2O$.

The structure of $LiI \cdot 3H_2O$ has been examined by Hendricks with the following results[2]:

Hexagonal, C_{6v}^4 or D_{6h}^4, $a = 7.45$, $c = 5.45$, $c/a = .731$, $Z = 2$ $(LiI \cdot 3H_2O)$.

$2\,I$ in $\frac{1}{3}\frac{2}{3}0$; $6\,O$ in $u\bar{u}v$.

Absent reflections $hh.l$ with l odd.

These conclusions I have confirmed with oscillation and powder photographs, and a basal Laue photograph, all in Mo radiation. For these exposures suitable specimens were sealed into glass tubes.

The similarity between $LiClO_4 \cdot 3\,Aq$ and $LiI \cdot 3\,Aq$ suggests that the water molecules occupy similar positions in the two crystals. To test

this point I have compared observed and calculated intensities for the iodide; and the results, while not so conclusive as in the preceding case, assuredly do not conflict with such a structure.

An estimate of u may be obtained from the relative intensities (on c-axis oscillation photographs) of reflections $hk.0$ when $2\,h + k \neq 3\,m$, on which the oxygen lattice has an appreciable effect. By the usual methods u may be restricted to the range $50 \pm 5°$ in the region $30° < u < 90°$. The fact that the intensities repeat themselves as 1 varies by 2 suggests that $v = 0$ or $\frac{1}{2}$. The observed intensity $50.1 \sim 50.0$, whereas in general $hk.1 \gg hk.0$ (with $2\,h + k \neq 3\,m$), shows that $v = \frac{1}{2}$. The tabulated intensities are calculated with $u = 51°$, $v = 180°$. These values give satisfactory agreement between calculated and observed intensities on a powder photograph, while the omission of the oxygen lattice from the calculated amplitude gives a definite conflict. No structure with the iodines in hexagonal close packing will account for the observed intensity of 30.1, which was found, in agreement with Hendricks, to be unduly strong.

This structure differs from the foregoing $LiClO_4 \cdot 3\,H_2O$ only in the substitution of spherical iodine atoms for tetrahedral ClO_4 groups. The same substitution of ClO_4 for I has previously been observed, for example, in several cobaltammines and also in the cubic alkali compounds $MeI—MeClO_4$.

For the lithium ions, which cannot be located by intensity data, three sets of points are available; these are $\frac{1}{3}\frac{2}{3}\frac{1}{2}$, $\frac{2}{3}\frac{1}{3}0$ (as proposed by Hendricks), 000, $00\frac{1}{2}$ and $00\frac{1}{4}$, $00\frac{3}{4}$. A parallel option was found in the similarly constructed crystal $LiIO_3$[1]) which differs in composition from the present compound by the substitution of oxygen for water. If Li is at $00\frac{1}{4}$, $00\frac{3}{4}$ the $Li—O$ coordination in the two compounds will be the same; accordingly this point is to be preferred if the iodate structure is accepted. This places each Li at the center of a nearly regular octahedron of oxygens at a distance 2.14, the successive octahedrons along the c-axis sharing faces as in the iodate, with the $Li—Li$ distance in this direction $c/2$ or 2.72. Each Li is also at the center of a flattened iodine octahedron at a distance 4.50. Each iodine is surrounded by twelve oxygens at a distance 3.70—3.75.

If this structure is correct, it can no longer be considered isostructural with the triethyl ammonium halides. It has been stated[2]) that here the nitrogens are in $\frac{1}{3}\frac{2}{3}u$ between halogens on the same c-axis; such a change

1) W. H. Zachariasen, F. Barta, Physic. Rev. **37**, 1626. 1931.

2) S. B. Hendricks, Z. Krist. **67**, 472. 1928.

in position probably accounts for the increase in axial ratio ($c/a = .87$ as compared to .73 for the iodide).

Summary: There are two formulas of $LiI \cdot 3\,H_2O$ in the hexagonal unit $a = 7.45$, $c = 5.45$, $c/a = .731$. This unit is similar to that of $LiClO_4 \cdot 3\,H_2O$. Evidence is presented that the atomic positions in space group C_{6v}^4 are

$2\,Li$ in $00\frac{1}{4}$.

$2\,I$ in $\frac{1}{3}\frac{2}{3}0$.

$6\,Aq$ in $u\bar{u}v$ with $u = 51°$, $v = 180°$.

This structure also resembles that of $LiIO_3$ from which it differs in composition only by the substitution of water molecules for oxygen atoms.

Table II. c-Axis Oscillation Photographs of $LiI \cdot 3\,H_2O$.

$hk \cdot 0$	(F)	Intensity		$hk \cdot 1$	(F)	Intensity	
		W	H			W	H
10.0	32	m	st	10.1	72	vst	mst
20.0	63	mst	mst	20.1	103	vst	m
21.0	48	mst		21.1	56	st	
31.0	33	m		31.1	62	st	
40.0	45	w	w	40.1	72	st	mst
32.0	18	0		32.1	58	mst	
50.0	40	w	vw	50.1	41	mw	w
42.0	33	vw		42.1	59	m	
51.0	34	w	vw	51.1	53	m	mw
43.0	24	0		43.1	42	w	

The second column gives values of (F) calculated for the oxygen parameters $u = 51°$, $v = 180°$, and for the iodine positions as stated, with the use of the scattering curves of James and Brindley. The fourth column gives the intensities published by Hendricks, which in some respects deviate from the present intensities as given in the third column.

$Ba(ClO_4)_2 \cdot 3\,H_2O$.

From Laue, oscillation and powder photographs the symmetry of this crystal is that of C_{6h}, the departure from D_{6h} being only apparent in a few weak spots with l odd on a basal Laue photograph. The lattice constants are

Hexagonal, C_6^6 or C_{6h}^2, $a = 7.28$, $c = 9.64$, $c/a = 1.32$,
        density $= 2.91$, $Z = 2$.

From literature $c/a = 1.325$, density $= 2.91$[1]), symmetry class not assigned.

Characteristic absences $00.l$ with l odd.

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1) Wulff, Z. Krist. 77, 84. 1931.

On oscillation and Laue photographs reflections with 1 odd are relatively weak or absent; this at once indicates that Ba lies in $00u$, $00u + \frac{1}{2}$ precisely in the positions proposed for Li in the preceding compounds. A pseudo unit with $c' = c$ containing one formula of $Ba(ClO_4)_2 \cdot 3H_2O$ will be similar to the unit containing two formulas of $LiClO_4 \cdot 3H_2O$ after removal of half the water, a substitution of Ba for $2\,Li$, and a consequent contraction along vertical and horizontal axes such that c/a decreases from .70 to .66. This morphological similarity was remarked by Wyrouboff.

Comparison of Structural Units

	c	a	c/a
$2\,LiClO_4 \cdot 3H_2O$	5.42	7.71	.704
$2\,LiI \cdot 3H_2O$	5.45	7.45	.731
$Ba(ClO_4)_2 \cdot 3H_2O$	4.82	7.28	.662

Optical Examination.

The refractive indices of the following lithium salts were measured by the immersion method with the use of a white light source.

	ω	ε	$\omega - \varepsilon$
$LiI \cdot 3H_2O$	1.655	1.625	.030
$LiClO_4 \cdot 3H_2O$	1.483	1.448	.035
$Ba(ClO_4)_2 \cdot 3H_2O$[1])	1.533	1.532	.001

Thus these two lithium salts are optically as well as structurally similar.

After long standing in the presence of its saturated solution, well formed short thick colorless prisms of $LiI \cdot 3H_2O$ were found. These presented the faces $10\bar{1}0$, a pyramid $h0hl$, and probably a second pyramid in another zone; the Laue photograph previously referred to was obtained with one of these prisms.

Crystals of $LiI \cdot 3H_2O$ are plastic and have no cleavage. Basal sections obtained by cutting with a sharp edge always give a distorted interference figure due to deformation; cleavage sections of the perchlorate give a perfect uniaxial negative cross.

$LiNO_3 \cdot 3H_2O$ crystallises in biaxial negative prisms with parallel extinction. The principal indices are 1.523, 1.490 and 1.365, with β parallel to the prism axis, and with $2\,V \sim 55°$.

Some of the foregoing photographs of $LiI \cdot 3H_2O$ were prepared at the Ryerson Laboratory of the University of Chicago, where I had the privilege of discussing these structures with Professor W. H. Zachariasen.

1) Data of Wulff, Z. Krist. 77, 84. 1931.