THE CRYSTAL STRUCTURE OF LITHIUM IODIDE TRIHYDRATE.

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The halides of lithium form hydrates, ammoniates and alkyl ammoniates the regions of stability of which are partially known. The equilibrium diagrams for the systems $LiCl$-H_2O, $LiBr$-H_2O and Li-H_2O as determined by G. F. Hüttig and W. Steudemann[1] are shown in Fig. 1. From this figure it can be seen that $LiCl.H_2O$, $LiBr.2H_2O$ and $LiI.3H_2O$ are the stable phases at room temperatures. The crystal structure of $LiCl.H_2O$ has been determined.[2] The purpose of the present investigation was to determine the crystal structure of $LiI.3H_2O$ or of $LiBr.2H_2O$.

The lithium halide was prepared by the action of the halogen acid upon lithium carbonate. Crystals were grown from the aqueous solutions by desiccation over sulfuric acid. Optical examination of the crystals of $LiBr.2H_2O$ showed them to be biaxial. This compound was not examined further. Crystals of $LiI.3H_2O$ proved to be extremely plastic and deliquescent. It was possible to bend a single crystal through an angle of 270° without producing a visible fracture. Undeformed crystals were uniaxial in character while the deformed ones gave distorted uniaxial figures which could have been confused with biaxial figures. The previous description of this compound as forming optically biaxial crystals[3] might have resulted from an examination of deformed crystals.

The developed crystals were apparently hexagonal prisms elongated in the c direction. A Laue photograph made with the incident X-ray beam normal to one of the prism faces shows a two-fold axis and two planes of symmetry. This observation requires the crystals to be hexagonal rather than tetragonal with an atomic arrangement isomorphous with point group 6d; 6e, 6D or 6Di.

Laue photographs were made with the incident X-ray beam normal to (010) and making small angles with this normal. Spectrum photographs were made with (010) and (001) as the principal reflecting faces being initially parallel to the X-ray beam and oscillated through an eagle of 20° about

[1] Z. Phys. Chem. **126**, 105-117, 1927.
[2] Hendricks, S. B., Zeit. f. Krist. **66**, 297 (1927).
[3] Troost, Ann. Chim. Phys. (3) **51**, 126, 1857.

some crystallographic direction. The smallest unit of structure compatible with the Laue data listed in Table II and the spectrum data of Table I and Fig. 2 has $d_{100} = 7.45$ Å and $d_{001} = 5.45$ Å. The density calculated on the basis of such a unit containing two $LiI.3H_2O$ is 2.375. The density experimentally determined by the suspension method of Retgers (bromoform-alcohol mixtures being used) is 2.29. This latter value might be in error due to the difficulty encountered in drying the crystals and on account of their solubility in the suspending media.

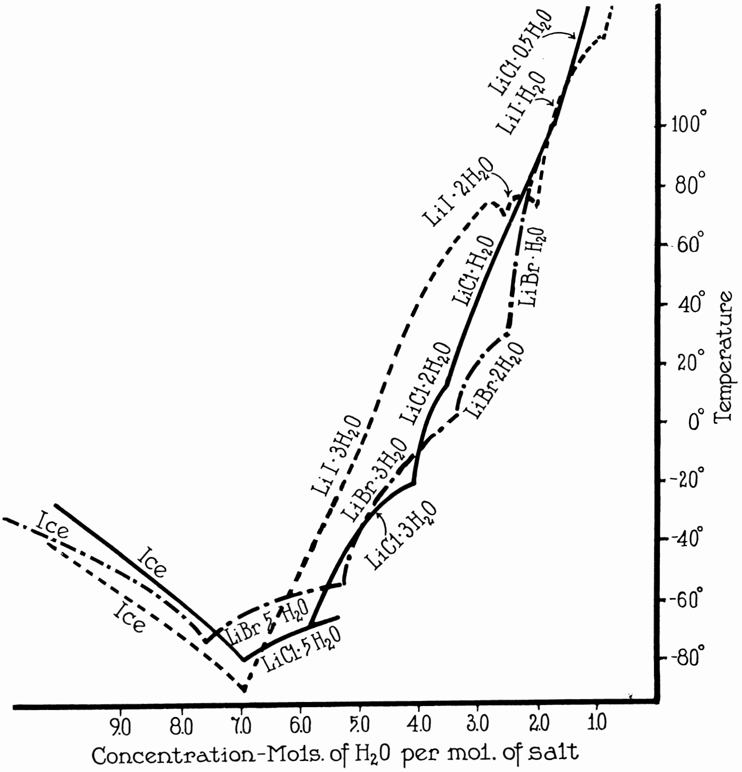

Fig. 1. Equilibrium diagrams for the systems $LiX–H_2O$ (X = Cl, Br, I) after Hüttig and Steudemann.

The only space groups isomorphous with point groups 6Di, 6D, 6e or 6d giving possible positions for two $LiI.3H_2O$ in the unit of structure are 6Di-1, 6Di-2, 6Di-3, 6Di-4, 6D-1, 6D-6, 6e-1, 6e-2, 6e-3, 6e-4, 6d-1, 6d-2, 6d-3 or 6d-4. Of the space groups listed above only 6e-4, 6Di-4, and 6D-6 account for the absence of odd order reflections from (001) (Table I) and the observed very low intensity of reflection from (031) and quite strong reflections from (021) and (041) (Fig. 2). The atomic arrangement derivable from 6D-6 with H_2O at (g)[4] would be quite unlikely chemically since it would lead to a $3H_2O$ group not associated with the iodine or lithium atom. The other possible arrangement resulting from 6D-6 or 6Di-4 are special cases of the more general arrangement derivable from 6e-4. The possible arrangements for two $LiI.3H_2O$ in this space group are:

TABLE I. Typical Spectrum Photographic Data from Lithium Iodide Trihydrate. Mo K Radiation.

Plane	Line	Order	d_{hkl} Å/n	Observed Intensity	$\sqrt{s}$ Calculated for Iodine Atoms
001(1)	mo $K\beta$(2)	2	5.41	m.s.	
	α_1	2	5.45	v.s.	2.00 x $\bar{1}$
	β	4	5.41	m.w.	
	α_1	4	5.42	m.s.	2.00
010	β	2	6.48	m.w.	
	α_1	2	6.50	m.s.	1.00
	β	3	6.49	m.	
	α_1	3	6.46	s.	2.00
	α_1	4	6.46	w.	1.00

(1) NaCl was used as a reference substance in the determination of the interplaner spacings for (001).

(2) The following wave lengths were used in the calculations, mo $K\beta$, $\lambda = .6311$Å; mo $K\alpha_1$, $\lambda = .7078$Å.

(a) $00u;\ 0,0,u+\frac{1}{2}.$ (b) $\frac{1}{3}\frac{2}{3}u;\ \frac{2}{3},\frac{1}{3},u+\frac{1}{2}.$

(c) $u\bar{u}v;\quad 2\bar{u},\bar{u},v;\quad u,2u,v;$

$\bar{u},u,v+\frac{1}{2};\ 2u,u,v+\frac{1}{2};\ \bar{u},2\bar{u},v+\frac{1}{2}.$

If two atoms, lithium or iodine, were in positions (a) their maximum distance apart would be 2.72Å, which is improbably small for the iodine atoms. Such an arrangement would amount to an association of ions of like charge in the unit of structure. It is more probable that both the iodine and lithium atoms are at (b) with different values of the parameter. In order to account for the presence of reflection from (031) the oxygen atoms of the H_2O molecules must be at (c).

The extremely low scattering powers of the lithium atoms and oxygen atoms of an H_2O molecule relative to that of the

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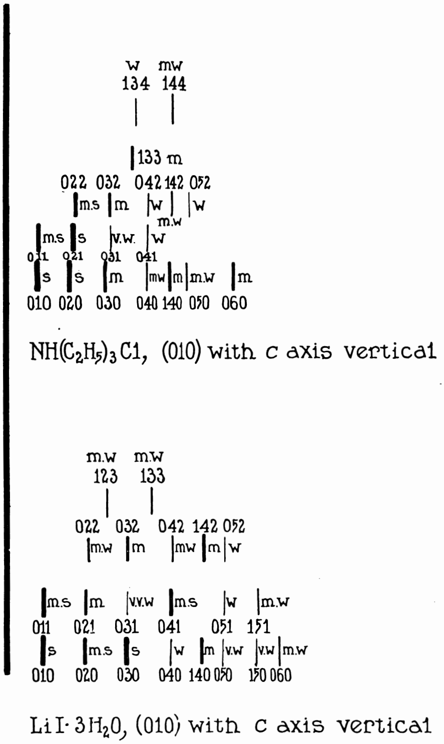
[4] Wyckoff, R. W. G., The Analytical Expression of the Theory of Space Groups, p. 166. Washington, 1922.

iodine atoms makes an evaluation of the parameters impossible at the present time. The presence of a reflection from (031) of very low intensity (Fig. 2) indicates that the oxygen atoms do have a slight effect upon the intensity of reflection. In order that the oxygen to oxygen distance should not be less than 1.0 Å, u_0 must be between .04-.29.



$NH(C_2H_5)_3Cl$, (010) with c axis vertical

$LiI \cdot 3H_2O$, (010) with c axis vertical

Fig. 2. A partial reproduction of spectrum photographs from similarly oriented crystals of $LiI.3H_2O$ and $NH(C_2H_5)_3Cl$, mo $K\alpha_1$ lines alone being shown.

The agreement between the observed intensities of reflection and the calculated structure factors, iodine atoms alone being considered, is shown in Tables I and II.

It is to be noted in Table II that the reflection from (531) at $\lambda = .38$ is of much greater intensity than that from (323) at $\lambda = .35$ even though the planes have approximately the same interplaner distance and the same structure as far as iodine atoms alone are considered. The absorption edge for the element iodine is at λ = .3737Å. This is further confirmation for the correctness of the determination of the unit of structure.

TABLE II. Typical Laue Photographic Data from Lithium Iodide Trihydrate. Tungsten General Radiation, 52,000 V Peak.

Plane	d_{hkl} Å	nλ	Observed Intensity	$\sqrt{s}$ Calculated for Iodine Atoms
$\bar{1}13$(1)	1.742	.47	v.s.(2) (3)	1.73 x $\bar{1}$
103	1.742	.47	v.s.	1.73
$\bar{5}30$	1.471	.40	m.	1.00
$3\bar{1}3$	1.451	.32	m.w.–m.	1.73
$\bar{3}23$	1.451	.35	m.w.–m.	1.73
$\bar{5}31$	1.420	.38	m.s.	1.73
$5\bar{2}\bar{1}$	1.420	.29	m.w.–m.	1.73
$4\bar{1}3$	1.269	.47	s.	1.73
$6\bar{2}1$	1.183	.41	m.s.	1.73
$6\bar{2}\bar{1}$	1.183	.42	m.s.	1.73
$\bar{6}41$	1.183	.46	m.s.–s.	1.73
$7\bar{2}0$	1.027	.47	m.s.	2.00
205	1.028	.32	w.	1.73
$\bar{2}25$	1.028	.34	w.	1.73
$\bar{6}43$	1.007	.34	w.	1.73
$\bar{5}44$	.975	.46	m.s.	2.00
$7\bar{2}2$	.961	.41	m.–m.s.	2.00
$\bar{8}51$	.904	.28	v.v.w.	1.73
$6\bar{1}4$	.879	.47	v.w.	1.00
$8\bar{2}1$	.878	.46	w.	1.73

(1) The incident X-ray beam was approximately normal to (010).
(2) The following abbreviations are used throughout this paper; v.s., very strong; s., strong; m.s., medium strong; m. medium; m.w., medium weak; w., weak; v.w., very weak; v.v.w., very, very weak.
(3) It is to be remembered that the K absorption limit of iodine is at λ = .3737Å, for the element.

DISCUSSION.

The unit of structure containing two $LiI.3H_2O$ is shown in Fig. 3. In this figure the H_2O molecules are shown as associated with the lithium atom. It is impossible at the present time to eliminate the structure in which the H_2O molecules would be associated with the iodine atom. In the crystal structure determination of the previously studied $LiCl.H_2O$[5] it was definitely shown that the H_2O molecule was not associated with the chlorine atom, although it could not be proven that it was associated with the lithium atom. In the case of $LiI.3H_2O$ it is further possible that v_0 might be about one

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[5] Hendricks, S. B., Zeit. f. Krist. **66**, 297 (1927).

half of u_{Li} (u_{Li} being taken as zero) which would not require the presence of an $Li.3H_2O$ or an $I.3H_2O$ group in the unit of structure.

The space group and the resulting atomic configuration of lithium iodide trihydrate are the same as that of the previously studied triethyl ammonium halides.[6] This similarity is shown by writing the formula as $I(Li(H_2O)_3)$ and $I(NH(C_2H_5)_3)$.

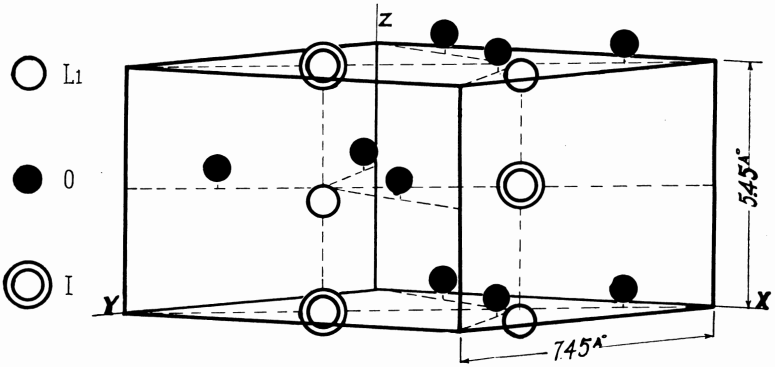

Fig. 3. The unit of structure containing two $LiI.3H_2O$.

The lithium atom can be considered as equivalent to the (NH) group while each H_2O molecule is equivalent to a (C_2H_5) group. We can thus have an $Li(H_2O)_3$ group which is structurally similar to the $NH(C_2H_5)_3$ group. This marked similarity in structure is indicated by the two spectrum photographs reproduced as Fig. 2.

This similarity between the geometrical configuration of the hydrates of lithium and the alkyl ammonium compounds is further shown in the case of $LiCl.H_2O$[7] and NH_3CH_3Cl,[8] the $(Li.H_2O)$ group being structurally similar to the (NH_3CH_3) group.

The Li-I distance is the only distance that can be considered on the basis of the present data. If the value of u_{Li} is one half, the Li-I distance is ca 2.72A. In the case of the previously studied anhydrous lithium iodide[9] the Li-I distance is ca 3.00 Å if the structure is similar to that of sodium chloride.

[6] Hendricks, S. B., Zeit. f. Krist. (in press).
[7] Hendricks, S. B., Zeit. f. Krist. **66**, 297, 1927.
[8] Hendricks, S. B., Zeit. f. Krist. (in press).
[9] Ott, H., Phys. Zeit. **24**, 209, 1923; Wyckoff, R. W. G., and Posnjak, E. W., J. Wash. Acad. Sci. **13**, 393, 1923.

This distance is in agreement with the value 2.76 recently given by Pauling[10] as the distance to be expected between the centers of spherical Li^+ and I^- ions in contact.

CONCLUSIONS.

The crystal structure of lithium iodide trihydrate has been determined by the use of Laue and spectrum photographs. The hexagonal unit of structure containing two $LiI.3H_2O$ has $d_{100} = 7.45$ Å and $d_{001} = 5.45$ Å. The space group is 6e-4.

The atomic positions are:

I at (b) $\frac{1}{3}\frac{2}{3}u$; $\frac{2}{3},\frac{1}{3},u + \frac{1}{2}$ (with $u = 0$);
Li at (b) $\frac{1}{3}\frac{2}{3}u$; $\frac{2}{3},\frac{1}{3},u + \frac{1}{2}$; O at (c)
$u\bar{u}v$; $2\bar{u},\bar{u},v$; $u,2u,v$;
$\bar{u},u,v + \frac{1}{2}$; $2u,u,v + \frac{1}{2}$; $\bar{u},2\bar{u},v + \frac{1}{2}$.

It was impossible to determine the values of the parameters.

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[10] Pauling, L., J. Am. Chem. Soc. 49, 765, 1927.