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CRYSTAL STRUCTURE OF LITHIUM IODATE

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ABSTRACT

The structure of lithium iodate was determined by using the oscillation and powder methods. Lithium iodate is hexagonal with 2 molecules per unit cell of $a=5.469\pm 0.003$A, $c=5.155$A ± 0.005A. The space group assigned is D_6^6 and the atom positions are: 2Li in (001/4) (003/4), 2I in (1/3 2/3 1/4) (2/3 1/3 3/4) and 6 O in $(uu0)$ $(0\bar{u}0)$ $(\bar{u}00)$ $(\bar{u}\bar{u}\frac{1}{2})$ $(0u\frac{1}{2})$ $(u0\frac{1}{2})$ with $u=1/3$. The structure is based on hexagonal closest packing, with the lithium and iodine atoms both lying within oxygen octahedra. The atomic distances are Li$-$O and I$-$O$=2.23$A with lithium octahedra sharing faces with each other, one lithium and one iodine octahedra sharing only edges and two iodine octahedra only corners.

LITHIUM iodate is the only member of the alkali iodates, whose structure has not yet been determined.[1] In searching the literature no information was found regarding its crystallographic properties. A microscopic examination of the fine crystalline material of chemically pure $LiIO_3$ as furnished by Kahlbaum, showed that the crystals were short hexagonal prisms. Though $LiIO_3$ does not crystallize in very large crystals, two crystal splinters were found sufficiently large to be used for the oscillation method. Both crystals were hexagonal prisms and photographs were taken using the principal directions as axes of rotation. In view of the fineness of the material a large number of powder photographs were taken using Mo$K\alpha$, Cu$K\alpha$, and Fe$K\alpha$, radiation.

The photographs were worked out in the usual manner and lead to the following dimensions of the hexagonal cell.

$$a=5.469\text{A}\pm 0.003\text{A} \qquad c=5.155\text{A}\pm 0.005\text{A} \qquad c/a=0.9427$$

A rough density determination of $LiIO_3$ gave 1.9 molecules equivalent to 2 molecules per unit cell. The calculated density is 4.48. The greater part of the observations is compiled in Tables I and II. From the tables it is clearly seen that a rhombohedral cell is impossible because of the observed reflections. (The number of molecules in the hexagonal cell also exclude a rhombohedral lattice.) Since the oscillation photographs did not show any deviation from full hexagonal symmetry, consideration of the space group was limited to the following classes: D_{6h}^n, D_6^n C_{6V}^n and D_{3h}^n. Of these D_6^2 and D_6^5 were ruled out because they have no 2-fold (or 1-fold) positions.

Tables I and II show that whenever $2h+k$ is divisible by 3, exceptionally strong reflections are observed if l is even; whereas the intensity is weak or

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[1] V. M. Goldschmidt, Vid. Akad. Skr. Oslo **2,** 79 (1926) KIO_3, $RbIO_3$; W. H. Zachariasen, ibid. **4,** 100, 106 (1928) $NaIO_3$, $CsIO_3$.

nil if l is odd. This observation can only be accounted for by putting the two iodine atoms in positions corresponding to a hexagonal closest packing of these atoms. The only available space groups compatible with such an arrangement are D_{3h}^1, D_{3h}^4, C_{6V}^4, D_6^6, and D_{6h}^4. The space groups D_{6h}^4, C_{6V}^4,

TABLE I. *Oscillation photographs.*

hk. l	$\sin\theta$	$\lvert F\rvert$	Int.
00.1	0.0687	nil	nil
10.0	.0748	43.6	m
10.1	.1015	78.7	vs
11.0	.1295	72.1	vs
00.2	.1373	55.4	s
11.1	.1466	25.5	w
20.0	.1496	37.4	m
10.2	.1564	36.9	m
20.1	.1645	65.4	s
11.2	.1877	86.6	s
21.0	.1977	33.8	vw
20.2	.2030	33.8	w
00.3	.2061	nil	nil
21.1	.2093	64.2	m
10.3	.2192	61.5	s
30.0	.2244	90.8	s
30.1	.2345	nil	nil
21.2	.2408	31.2	w
11.3	.2433	14.6	nil
20.3	.2545	57.1	m−
22.0	0.2590	60.8	m
30.2	.2629	53.0	m
22.1	.2679	13.5	nil
31.0	.2695	30.4	vw
00.4	.2746	73.8	m
31.1	.2781	53.7	m−
21.3	.2856	54.6	m
22.2	.2932	68.0	m
31.2	.3024	28.0	vw
11.4	.3036	56.0	m
32.0	.3258	27.0	vw
32.1	.3330	49.5	w
41.0	.3343	53.4	w
31.3	.3392	49.2	w−
41.1	.3413	9.4	nil
32.2	.3536	26.4	vvw
41.2	.3614	61.1	w
32.3	.3854	46.0	w
41.3	.3926	7.3	nil

TABLE II. *Powder photographs.*

			Int. Obs.	
hk. l	$\sin\theta$	$\lvert F\rvert^2xf$	Mo	Cu
00.1	0.0687	nil	nil	nil
10.0	.0748	1.9	w+	w
10.1	.1015	12.4	vs	s
11.0	.1295	5.2	ms	m
00.2	.1373	1.0	vw	vw
11.1	.1466	1.3	w	vw
20.0	.1496	1.4		
10.2	.1564	2.7	w	w
20.1	.1645	8.6	ms	m
11.2	.1877	15.0	s	s
21.0	.1977	2.3	vw	w
20.2	.2030	2.3	vw	w
00.3	.2061	nil		
21.1	.2093	16.5	s	s
10.3	.2192	7.6	m−	m−
30.0	.2244	8.2	m	m−
30.1	.2345	nil	nil	nil
21.2	0.2408	3.9	w+	w
11.3	.2433	.4		
20.3	.2545	6.5		m
22.0	.2590	3.7		w+
30.2	.2629	5.6		m
22.1	.2679	.4		vw
31.0	.2695	1.9		
00.4	.2746	1.8		nil
31.1	.2781	11.5		s
10.4	.2847	1.7		s
21.3	.2856	12.0		
22.2	.2932	9.2		m
40.0	.2992	.8		
31.2	.3024	3.1		ms
11.4	.3036	6.3		
30.3	.3045	nil		
40.1	.3069	5.4		w

TABLE III. *F Curves* (*MoKα*).

$\sin\theta$	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40
Li	2.0	1.9	1.8	1.6	1.3	1.1	.85	.7
I	50	45.5	41	37	33.5	31	28	26
O	8.0	7.5	4.9	3.0	2.7	2.1	1.6	1.3

The F-curve for iodine was calculated by Thomas' method, the one for oxygen is the experimental one found by J. West in KH_2PO_4.

and D_{3h}^4 are ruled out because they require that the odd order reflections from all planes $h\ k.l$ where $2h+k=3n$ and l odd shall be missing, and while many of these reflections are not found, there is evidence in the photographs that some of them are definitely present. This limits the space group selection to D_{3h}^1 and D_6^6.

In D_{3h}^1 in order to have hexagonal closest packing the necessity for unequivalent iodine atoms arises. The possibility that all oxygen atoms lie in the same plane is unreasonable as that would give too small oxygen to oxygen distances. Likewise this rules out the possibility that they all lie on 3-fold or 6-fold axis of symmetry. The only possible arrangements of the 6 oxygens are therefore: $3j+3k$ or $6n$ with $v=1/4$. None of these possibilities leads to reasonable structures.

In case the 6 oxygens are put in $3j+3k$ and the required oxygen to oxygen distance is greater than 2.50A, the iodine to oxygen distance is smaller than 1.72A. It seems improbable that the oxygen to oxygen distance is smaller than 2.50A, and that the iodine to oxygen distance is as small as 1.72A. This arrangement must therefore be ruled out and for similar improbabilities placing the 6 oxygens in positions $6n$ can not be considered.

As an additional support for ruling out the considerations of the previous paragraph are the intensity considerations. With the oxygen in $3j+3k$ it is impossible to explain the weak 00.2 reflection. Similarly if the oxygens lie in $6n$ the parameter v must be 1/4 in order to explain the absent odd orders from the basal plane, which would necessitate the absence of reflections 11.1, which as the tables show are definitely present.

The only remaining space group is D_6^6.

The 2 iodine atoms are put in positions (1/3, 2/3, 1/4) (2/3, 1/3, 3/4) in accordance with the required hexagonal closest packing. Since all the atoms can not lie on the 3-fold axes of symmetry, the only positions for the oxygens are $(uu0)$ $(0\bar{u}0)$ $(\bar{u}00)$ $(\bar{u}\bar{u}\tfrac{1}{2})$ $(0u\tfrac{1}{2})$ $(u0\tfrac{1}{2})$ or $(u\bar{u}\ 1/4)$ $(2\bar{u}\bar{u}\ 1/4)$ $(u2u\ 1/4)$ $(\bar{u}u\ 3/4)$ $(2uu\ 3/4)$ $(\bar{u}2\bar{u}\ 3/4)$. The latter arrangement does not account for the relative weak 00.2 reflection and therefore the first set is the correct one.

An accurate determination of the oxygen parameter cannot be made due to the small scattering power of these atoms in comparison with that of iodine. The powder photographs show that 30.0 and 30.2 occur with nearly the same intensity although the latter form has twice as many faces as the former. In order to explain this ratio the oxygen atoms must give a large positive contribution to the structure factor for both reflections. This requirement necessitates $u=1/3$. The value 1/3 is very probable as that gives us hexagonal close packing of the oxygens. A close packed arrangement of the oxygens (using oxygen to oxygen distance $=2.7$A) would give us a cell of dimensions $a=4.68$A, $c=4.42$A with an axial ratio of 0.944. The fact that the experimental cell is larger than the theoretical one must be attributed to an expansion of the close packing due to the circumstance that both iodine and lithium are too large to fit in the interstices.

The lithium atoms are so light that their positions cannot be determined from the intensities of reflections. There are three sets of available positions for lithium: (2a) (000) $(00\frac{1}{2})$; (2b) (00 1/4) (00 3/4) and (2d) (1/3, 2/3, 3/4) (2/3, 1/3, 1/4). The set (2a) will put lithium inside of an oxygen triangle with lithium to oxygen distance = 1.83A. Using (2b) or (2d) lithium will be within an octahedron of oxygens; the lithium to oxygen distance being 2.23A. The triangular arrangement of oxygens around lithium has never been found in other structures. Lithium either goes inside a tetrahedron of oxygens (Li_2O, $KLiSO_4$, Li_2MoO_4) or within an octahedran ($LiNO_3$). Of the latter two arrangements (2b) is the most plausible one, because this results in a lithium to iodine distance of 3.16A whereas (2d) would give 2.58A.

The complete structure thus determined is 2 Li in (00 1/4) (00 3/4), 2I in (1/3 2/3 1/4) (2/3 1/3 3/4) and 6 O in $(uu0)$ $(0\bar{u}0)$ $(\bar{u}00)$ $(\bar{u}\bar{u}\frac{1}{2})$ $(0u\frac{1}{2})$ $(u0\frac{1}{2})$ with $u = 1/3$. The intensities calculated on the basis of this structure agree well with the observed ones, as will be seen from the tables.

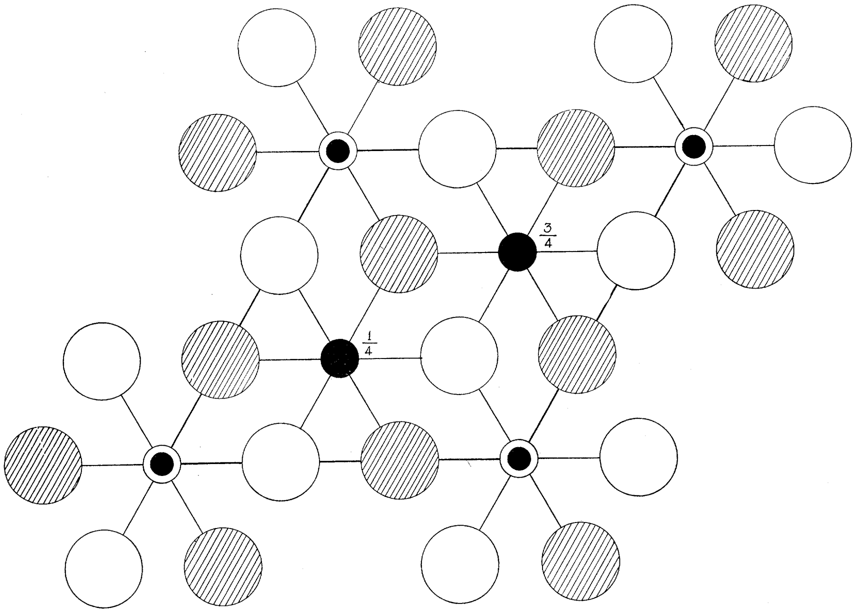

Fig. 1. Projection on the *c*-face of the structure of $LiIO_3$. The large circles represent oxygens at height 0. The large shaded circles represent oxygens at height *c*/2. The small solid circles represent iodine. The small solid centered circles represent lithium at height *c*/4, 3*c*/4.

Discussion of the Structure

In Fig. 1 is given a projection of the basal plane. The arrangement is a typical coordination lattice, of the hexagonal closed packed type met with in so many cases.

Almost perfect octahedra of oxygen atoms surround the iodine and lithium atoms. The IO_6-octahedra share only corners with each other. Sharing of the octahedral edges occur between IO_6 and LiO_6-polyhedra; while the LiO_6-octahedra share faces with each other. This result is in perfect agreement with what one should expect: The higher charges the central cations have, the fewer are the number of shared corners between two polyhedra.

Although the lithium positions have not been determined from intensity considerations, there is not much doubt about the positions assigned to these atoms. In $LiNO_3$, where Li also lies inside an octahedron of oxygens, it was found that the lithium to oxygen distance = 2.15A. In $LiIO_3$ the lithium to oxygen distance is 2.23A.

The distance iodine to oxygen is also 2.23A. For comparison the iodine to oxygen distance in other crystals of the same coordination number is given. $KIO_3-2.23$A; $RbIO_3-2.26$A, $CsIO_3-2.33$A.

The shortest oxygen to oxygen distance is 3.16A. In a previous paper by W. H. Zachariasen[2] it was shown that groups $(XO_3)^{-m}$ have an unsymmetrical structure if $v=3\times 8+2$(v being the total number of valence electrons in the group). In the (IO_6) group there are $50=6\times 8+2$ electrons. So that from reasons of analogy it would not be astonishing to find asymmetry in the IO_6 group. This asymmetry probably would result in a slight displacement of iodine away from the center of the octahedron in the direction of one face. However no observations pointing in that direction were observed. The possibility of detecting very small displacements is only possible with extremely accurate intensity determinations.

SUMMARY

Lithium iodate was examined by the oscillation and powder methods. The crystals were found to be hexagonal with 2 molecules in the cell $a=5.469$A ± 0.003A; $c=5.155$A$\pm$ 0.005A, $c/a=$ 0.9427. The calculated density is 4.48.

The space group was found to be D_6^6 with 2 Li in (001/4) (003/4). 2 I in (1/3 2/3 1/4) (2/3 1/3 3/4) and 6 O in $(uu0)$ $(0\bar{u}0)$ $(\bar{u}00)$ $(\bar{u}\bar{u}\frac{1}{2})$ $(0u\frac{1}{2})$ $(u0\frac{1}{2})$ with $u=1/3$.

The structure is based on the hexagonal closest packing. The lithium and the iodine atoms are both lying within oxygen octahedra. The distances Li-O and I-O are both 2.23A[3]. 2 lithium octahedra share faces with each other, one lithium and one iodine octahedra share only edges, two iodine octahedra only corners.

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[2] W. H. Zachariasen, Phys. Rev. **37,** 775 (1931).

[3] It is probably that a value of u slightly less than 1/3 is more correct, say $u=0.314$ which gives Li$-$0 2.15A and I$-$0$=$2.28A.