The Crystal Structure of Lithium Sulphate Mono-Hydrate, $Li_2SO_4 \cdot H_2O$.

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(With 2 figures.)

Introduction. The crystal structure of $Li_2SO_4 \cdot H_2O$ was investigated in order to determine the role of H_2O, because the atomic numbers are favorable, crystals easily obtained by evaporation from water solution at room temperature, and the crystallographic data[1]) well known. The complete structure was determined with data from rotating crystal photographs obtained with molybdenum radiation, which were checked whenever possible by means of Laue photographs.

Unit Cell and Space Group. The X-ray data led to the monoclinic cell, $a = 5.43$ Å, $b = 4.83$ Å, $c = 8.14$ Å, $\beta = 107°35'$, containing 1.977, that is 2 molecules. The calculated density is 2.075 while the observed is 2.052. This unit cell is not the same as the cell associated with the crystallographic axial ratio[1]). The equations of transformation from the crystallographic indices to the X-ray indices are as follows:

$$h = -l'$$
$$k = k'$$
$$l = \tfrac{1}{2}h' + \tfrac{1}{2}l'$$

Where h, k, and l are the X-ray indices, and h', k', and l' the crystallographic indices.

The agreement between the X-ray unit cell dimensions and the axial ratio, $a : b : c = 1.606 : 1 : 0.5633$, is shown by the corresponding X-ray unit cell ratio, $[\bar{2}01] : b_0 : \tfrac{1}{2} a_0 = 1.609 : 1 : 0.5624$.

The X-ray angle $\beta = 107°35'$ agrees with $72°32'$ the optically measured angle between crystallographic (100) and $(10\bar{1})$ faces.

Space Group. Graphical indexing[2]) of the plates and cylindrical films indicated that all classes of planes were present, except of the type $0k0$ when (k) is odd. Since $Li_2SO_4 \cdot H_2O$ is of the sphenoidal class[1]) all space groups except $C_2^1(P2)$, $C_2^2(P2_1)$, $C_2^3(C2)$ were eliminated directly. C_2^3 was eliminated because it is base centered and thus requires regular absences beyond those observed. C_2^1 was eliminated, at first

1) Groth, P., Chemische Krystallographie. Vol. 2, 362 (1908).
2) Bernal, J. D., Proc. Roy. Soc. London (A) **113** (1926) 117.

because it could not reasonably account for the regular absence of $0k0$, k odd, and finally because of intensity considerations. Accordingly $C_2^2(P2_1)$, containing only the two fold general positions $(x,\ y,\ z;\ \bar{x},\ y + \frac{1}{2},\ \bar{z})$ is assigned as the space group.

Determination of the Structure. Since there are 8 different atoms in general positions the complete structure involves the determination of 24 parameters. The sphenoidal class permits one parameter in the (b) direction to be arbitrarly chosen as zero. Although the final values of the parameters are based on agreement between observed and calculated intensities the large number of parameters necessitated certain simplifying assumptions in order to obtain a first approximation to the final structure. The main assumption was that the sulphur is surrounded by a tetrahedron of oxygen with a S to O distance of approximately 1.50 Å. This is conservative in view of the large number of crystals that have SO_4 tetrahedra, and the fact that no highly charged cation, other than sulphur, is present to cause distortion. With a tetrahedral arrangement of O about S the possibility of complete or even large cooperation between the various O's is small. Hence as a first approximation the entire intensity was considered as being from S. In C_2^2 it is necessary to consider parameter values from $0°$ to $180°$ only, where $360° =$ unit cell dimension.

The large intensity of 005 indicates that S should be in the neighborho odof $0°$, $36°$, $72°$, $108°$, $144°$, or $180°$. The values $0°$, $36°$, $144°$ and $180°$ were eliminated because 004 is exceptionally weak. The values $72°$ and $108°$ are equivalent so long as no other atom has been located. Hence $z = 72°$ was taken as the first approximation of the z parameter for S. Since 400 has zero intensity the value of the x parameter of S must be in the neighborhood of $22°$ or $67°$; but with 101 and $\bar{1}01$ both strong and with $72°$ as the ideal parameter in the z direction the $67°$ region is the only possible one for S in the x directon. The value of the y parameter of S was arbitrarly chosen as zero. Hence the ideal parameters of S were $x = 67°$, $y = 0°$, and $z = 72°$.

The next step was that of finding the orientation of the oxygen tetrahedron surrounding the S. The strength and nearly normal decline of the $0k0$ reflections was taken as an indication that in the (b) direction the O's were as close to $y = O$ as possible for a tetrahedron. Other possibilities were eliminated because of intensity disagreement and too small distances between the O's of different SO_4 groups. The oxygen of the H_2O was located with certainty from intensity considerations

alone. After the oxygen atoms were approximately located the structure was examined for oxygen tetrahedra[1]) and octahedra[2]). Four different tetrahedra, but no octahedra were found. Li was tentatively placed at the centers of these tetrahedra and intensities calculated. The location giving the best agreement was accepted. The improvement in agreement upon adding the Li is naturally small.

Although it involved much work the values of the 23 parameters were varied by trial calculations until the most consistent agreement was obtained. The final set of parameter values is given in table I while table II gives a sample of the observed and calculated intensities in

Table I. Values of the parameters.

	x_0	y_0	z_0	x_0	y_0	z_0
S	75	0	— 76	1.13 Å	0.00 Å	— 1.72 Å
O_1	55	— 50	— 30	0.83	— 0.67	— 0.68
O_2	180	— 10	— 69	2.71	— 0.13	— 1.56
O_3	28	— 28	— 143	0.42	— 0.37	— 3.23
O_4	58	110	— 71	0.87	1.47	— 1.60
O_5	205	170	— 139	3.09	2.28	— 3.14
Li_1	— 25	195	— 139	— 0.38	2.61	— 3.14
Li_2	60	172	+ 1	0.90	2.31	+ 0.02

Table II. Observed and Calculated Intensities.

Sin θ	Index	Observed Intensity	Calculated Intensity F	Sin θ	Index	Observed Intensity	Calculated Intensity F
.0686	100	M	10.4	.0689	$\bar{1}01$	S	27.8
.1372	200	VVW	2.0	.0890	101	S	35.1
.2058	300	M +	28.2	.0931	$\bar{1}02$	S —	16.6
.2743	400	nil	0.4	.0939	011	S	25.3
.1471	020	S —	43.6	.1006	110	S	25.0
.2942	040	W	12.3	.1139	012	S —	17.2
.4413	060	W —	8.6	.1186	$\bar{1}12$	S —	26.8
.0436	001	W +	5.7	.1260	102	S	25.2
.0872	002	M +	19.8	.1278	$\bar{1}03$	M —	10.0
.1308	003	W	12.8	.1307	$\bar{2}01$	S —	42.8
.1744	004	VW	8.0	.1384	$\bar{2}02$	W	6.9
.2180	005	M +	28.0	.1499	013	M +	15.2
.2616	006	nil	4.4	*.1534	021	M —	7.5

* Rest of table omitted in order to save space in the Journal.

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1) Albright, J. G., Z. Kristallogr. 84 (1932) 150.
2) Zachariasen, W. H., Norske Vid. Akad. Skr. Oslo 4 (1928) 53.

terms of F, the structure factor. Atomic scattering powers were obtained from experimental "F" curves[1]).

Discussion of the Structure. X-ray data give no direct information regarding hydrogen, but a probable position, provided H has a fixed position, can be located from a consideration of the structure surrounding O_5, the O of H_2O. The nearest oxygen neighbor to O_5, outside of the oxygen tetrahedra surrounding Li_1 and of which O_5 is a member, is O_2. (See figures 1 and 2.) The O_5 is separated from the O_2 in its own unit cell by a distance of 2.96 Å, and from O_2 in the next cell by the same distance. The distances result in an O_2—O_5—O_2 angle of 108°. Now if H is placed on the line between O_5 and O_2 the resulting H—O—H angle of 108° is a reasonable value. No other position surrounding O_5 seemed likely.

The structure is characterized by tetrahedra of oxygen surrounding the sulphur and lithium atoms. The interatomic distances together with a comparison to previously determined structures is given below.

S-tetrahedra	S to O = 1.49 Å average	O to O = 2.43 Å average
Na_2SO_4[2])	S to O = 1.49	O to O = 2.43
Li_1-tetrahedra	Li_1 to O = 1.99 Å average	O to O = 3.24
Li_2-tetrahedra	Li_2 to O = 1.97	O to O = 3.15
Li_2SO_4[3])	Li to O = 1.97	O to O = 3.20

Minimum O to O distance, different SO_4 groups = 2.85 Å.

The Li_1 tetrahedron is composed of three oxygen atoms from three different SO_4 groups and of the one oxygen from the H_2O group, while the Li_2 is composed of four different SO_4 groups. The various LiO_4 tetrahedra share corners (see figures), but there is no sharing of edges or faces. The perfect cleavange along $\bar{1}01$ (Crystallographic 101) is accounted for by the weakness of the bonds crossing the $\bar{1}01$ direction as can be seen in figure 2.

Despite the large number of parameters, the agreement between calculated and observed intensities of reflections and the very reasonable interatomic distances indicate that the structure is reliable.

1) As experimental S and O "F"-Curves the values for P and O were used. Compare West, J., Z. Kristallogr. 74 (1930) 306. For Li see Havinghurst, R. J., Physic. Rev. 28 (1926) 869.

2) Zachariasen and Ziegler, Z. Kristallogr. 81 (1932) 92.
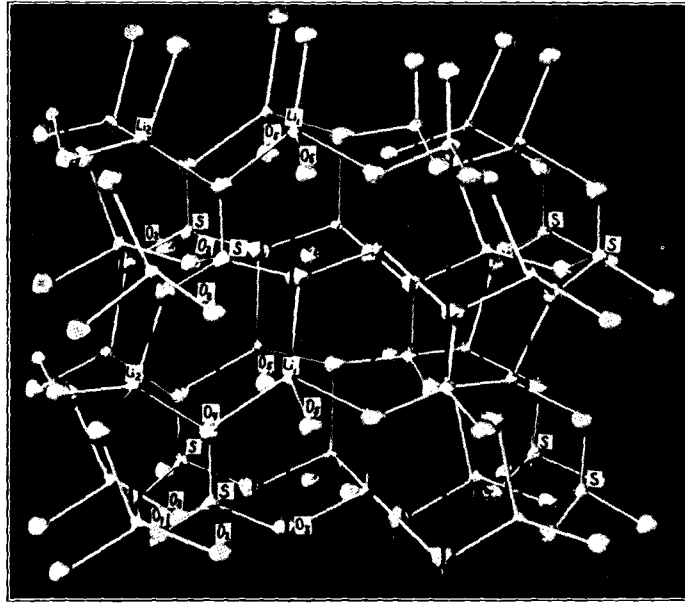
3) Albright, J. G., Z. Kristallogr. 84 (1932) 150.

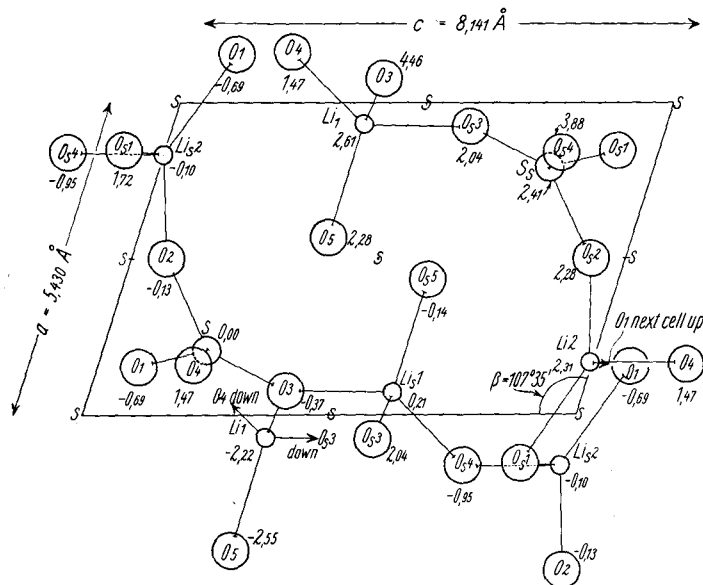Fig. 1. $Li_2SO_4 \cdot H_2O$. Photograph of model taken along the (a) axis, the (b) axis vertical.

Fig. 2. $Li_2SO_4 \cdot H_2O$. Projection of Structure on (b) face.

Summary.   Unit Cell: $a = 5.43$ Å, $b = 4.83$ Å, $c = 8.14$ Å
$$\beta = 107°35' \qquad 2 \text{ molecules.}$$

Space Group: $C_2^2(P\,2_1)$ (x, y, z) $(\bar{x}, y + \frac{1}{2}, \bar{z})$.

23 Parameters: Located first with the aid of simplifying assumptions and finally on agreement between calculated and observed intensities.

Structure: The O of H_2O is at one corner of an oxygen tetrahedron surrounding a lithium atom. H is in a probable position which yields an H—O—H angle of $108°$. Li and S atoms are surrounded by slightly distorted oxygen tetrahedra, with average distances as follows: S—$O = 1.48$ Å, O—$O = 2.43$ Å, Li_1—$O = 1.99$ Å, O—$O = 3.24$ Å, Li_2—$O = 1.97$ Å, O—$O = 3.15$ Å.