The final list of observed and calculated values of jF^2 is given in Table 1, the final parameters in Table 2.

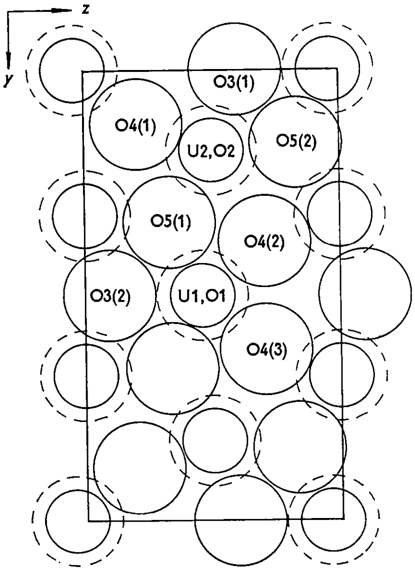

Fig. 4. The structure of U_3O_8 viewed along the *a* axis (representation as in Fig. 2). Numbers not in parantheses refer to parameters in Table 2 or equivalent sets; numbers added in parentheses allow reference to corresponding distances in Table 3.

The structure is shown in projection along the *a* axis in Fig. 4. From the list of interatomic distances (Table 3) it is seen that the U(1) and U(2) atoms are surrounded by six oxygen atoms at 2·07 to 2·23 Å. In addition, U(1) has a seventh oxygen atom at a somewhat larger distance (2·44 Å) while U(2) has its seventh atom at a much larger distance (2·71 Å). This seems in agreement with the assumption that U(1) may be identified with the U^{6+} ions and U(2) with the U^{5+} ions.

Table 3. *Interatomic distances*

	(Å)		(Å)		(Å)
U(1)–O(1)	2·07	O(1)–O(3)(2)	3·06	O(3)(1)–O(4)(1)	3·09
U(1)–O(3)(2)	2·44	O(1)–O(4)(2)	3·01	O(3)(2)–O(5)(1)	2·57
U(1)–O(4)(2)	2·18	O(1)–O(5)(2)	3·21	O(4)(1)–O(5)(1)	2·57
U(1)–O(5)(2)	2·23	O(2)–O(3)(1)	3·02	O(4)(2)–O(4)(3)	3·02
U(2)–O(2)	2·07	O(2)–O(4)(1)	2·97	O(4)(2)–O(5)(1)	2·55
U(2)–O(3)(1)	2·20	O(2)–O(4)(2)	3·42		
U(2)–O(4)(1)	2·12	O(2)–O(5)(1)	2·99		
U(2)–O(4)(2)	2·71	O(2)–O(5)(2)	3·02		
U(2)–O(5)(1)	2·16				
U(2)–O(5)(2)	2·20				

The author wishes to thank Dr. E. H. P. Cordfunke for providing the sample, P. C. Debets for the X-ray work and K. F. Maartmann-Moe for making the computer programs.

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The Crystal Structure of Lithium Hydrazinium Sulfate

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(*Received* 15 *April* 1963 *and in revised form* 12 *June* 1963)

At room temperature, lithium hydrazinium sulfate, $Li(N_2H_5)SO_4$, is orthorhombic, space group $Pbn2_1$, with $a=8{\cdot}99$, $b=9{\cdot}94$, $c=5{\cdot}18$ Å, and $Z=4$. The structure has been determined by X-ray diffraction and has been refined to give an R index ($\Sigma|F_o-F_c|/\Sigma|F_o|$) of 0·11. The lithium and sulfur atoms are at the centers of tetrahedra of oxygen atoms. The tetrahedra share apices to form a three-dimensional framework containing channels running parallel to the *c* axis. The hydrazinium ions lie in these channels and are linked into infinite chains by hydrogen bonding between their NH_2 groups. The electrical properties of the crystal appear to be related to the movement of protons within this chain.

Introduction

The interesting electrical properties of lithium hydrazinium sulfate, $Li(N_2H_5)SO_4$, have been described briefly by Pepinsky, Vedam, Okaya & Hoshino (1958). The crystals are orthorhombic, space group $Pbn2_1$, and are ferroelectric at room temperature, with a spontaneous polarization along the *c* axis. The spontaneous polarization is found to increase with temperature in the range −10 to +70 °C. Cuthbert & Petch

(1963) have shown that at room temperature the crystals conduct electricity strongly along the c axis, and that this conduction increases rapidly with temperature. They have also studied the behaviour of the nuclear magnetic resonance signals obtained from the crystal at different temperatures. Their results, together with those reported below, indicate how some of the electrical properties arise.

Structure determination

Lithium hydrazinium sulfate was prepared by the method of Sommer & Weise (1916) and crystals were grown by evaporation of the aqueous solution. The crystallographic data given below are compared with those reported by Pepinsky *et al.* (1958).

	This work	Pepinsky *et al.*
System	Orthorhombic	Orthorhombic
Space group	$Pbn2_1$ (C_{2v}^9)	$Pbn2_1$ (C_{2v}^9)
a	8·99 ± 0·01 Å	$8{\cdot}96_9$ Å
b	9·94 ± 0·01	$9{\cdot}91_3$
c	5·18 ± 0·01	$5{\cdot}17_8$
D_m	1·96 ± 0·01 g.cm^{-3}	1·966 g.cm^{-3}
D_c	1·95	
Z	4 × $Li(N_2H_5)SO_4$ per unit cell	
Absorption coefficient		
for Cu K radiation	62 cm^{-1}	
for Mo K radiation	6 cm^{-1}	
Systematic absences	$h0l$ $h+l=2n+1$ $0kl$ $k=2n+1$	

The crystals are elongated along the c axis with prominent (100), (110) and (101) faces. X-ray diffraction measurements were made at room temperature on a crystal which measured 0·1 × 0·1 × 1·0 mm along the three principal axes. The intensity data obtained with copper and molybdenum radiation were measured visually from Weissenberg films taken by rotation of the crystal about the c axis. The four layers, $l=0$, 1, 2 and 3, were scaled with the aid of precession photographs of the $0kl$ reflections. The intensities were corrected for Lorentz and polarization effects, but not for absorption or extinction.

The structure was solved with the aid of the Patterson function calculated with the $hk0$ data. The x and y coordinates were refined by Fourier and difference Fourier methods to give an R index ($R=\Sigma|F_o-F_c|/\Sigma|F_o|$) of 0·12. Coordinates in the z direction were then postulated, and all coordinates

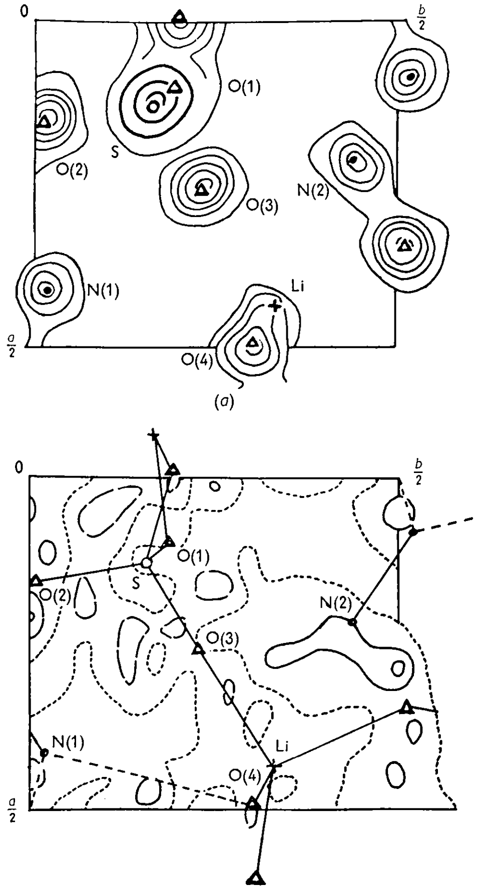

Fig. 1. (a) The electron density in lithium hydrazinium sulfate projected down the c axis. Contours are shown at intervals of 2 e.Å^{-2} except in the neighbourhood of the sulfur atom where they are shown at intervals of 10 e.Å^{-2}. Open circle: sulfur. Triangle: oxygen. Filled circle: nitrogen. Cross: lithium. (b) The electron density projected down the c axis after the atoms listed in Table 1 have been removed. Contours at intervals of $\frac{1}{2}$ e.Å^{-2}; positive contours are shown with a solid line, negative contours with a broken line, zero contour dotted. The hydrogen atoms have not been removed and should appear as positive electron density. The expected positions of hydrogen bonds are shown by dashed lines. Atomic positions are indicated as in (a).

Table 1. *Atomic parameters used in calculating the final set of structure factors shown in Table* 2

Species	x/a	y/b	z/c	B	Scattering factor
S^-	0·1286 ± 3	0·1579 ± 3	0·25	1·86 ± 6	Dawson (1960)
O(1)	0·106 ± 1	0·191 ± 1	0·519 ± 3	2·9 ± 2	Berghuis *et al.* (1955)
O(2)	0·154 ± 1	0·010 ± 1	0·220 ± 3	2·9 ± 2	
O(3)	0·259 ± 1	0·230 ± 1	0·149 ± 3	2·7 ± 2	
O(4)	0·497 ± 1	0·302 ± 1	0·596 ± 3	3·2 ± 2	
N(1)	0·418 ± 1	0·022 ± 1	0·746 ± 5	3·6 ± 3	
N(2)	0·217 ± 1	0·440 ± 1	0·742 ± 5	2·7 ± 3	
Li^+	0·437 ± 2	0·332 ± 2	0·253 ± 10	2·5 ± 4	Hurst (1960)

Scale factor (applied to F_c) = 0·235
The errors shown are the standard errors in the last decimal place

Table 2. *Observed and calculated structure factors*

In the least-squares refinement $F_o - F_c$ was weighted as $1/\sigma^2$ where $\sigma = 0{\cdot}3$ except for unobserved reflections where $\sigma = F_{\min}$

k	F_o	KF_c
	0k0	
0	-	61.0
2	5.2	6.9
4	6.8	6.2
6	12.4	11.2
8	2.2	2.4
10	1.8	2.1
12	2.8	2.5
14	<2.0	.7
	1k0	
1	7.8	8.2
2	9.3	10.1
3	17.9	18.5
4	11.5	11.2
5	8.9	8.5
6	1.7	1.5
7	2.2	2.0
8	3.0	3.0
9	3.0	2.9
10	<2.0	.8
11	<2.0	1.3
12	<2.0	.5
13	<2.0	1.2
14	2.5	2.2
	2k0	
0	2.8	2.4
1	14.5	15.0
2	3.4	3.3
3	.7	1.2
4	2.5	3.0
5	7.6	7.3
6	5.1	4.9
7	5.1	5.0
8	1.5	1.9
9	1.1	.8
10	1.4	1.9
11	2.7	3.0
12	<2.0	.4
13	<2.0	.6
14	<2.0	.5
	3k0	
1	6.4	6.0
2	11.4	9.9
3	.7	.8
4	.4	.2
5	2.4	2.3
6	1.4	1.3
7	7.7	6.8
8	5.2	5.0
9	1.4	1.6
10	<2.0	1.8
11	<2.0	.5
12	<2.0	.0
13	1.7	1.9
	4k0	
0	6.3	7.0
1	1.1	1.0
2	3.4	3.4
3	4.8	4.6
4	5.3	5.0
5	1.1	1.4
6	10.4	9.9
7	2.2	2.4
8	.4	.6
9	<2.0	1.3
10	1.5	2.0
11	<2.0	.4
12	1.6	2.5
13	<2.0	.3
	5k0	
1	2.4	2.7
2	7.4	6.8
3	6.6	6.2
4	2.5	2.9
5	<.3	.3
6	1.4	1.4
7	.7	.9
8	4.9	4.8
9	3.5	3.3
10	<2.0	2.3
11	<2.0	.4
12	<2.0	.6
	6k0	
0	1.7	1.7
1	8.2	8.1
2	1.4	1.6
3	1.5	1.8
4	1.4	1.0
5	6.5	6.3
6	1.7	1.8
7	3.5	3.3
8	<2.0	.2
9	<2.0	1.5
10	<2.0	.7
11	<2.0	1.9
12	<2.0	.2
	7k0	
1	6.7	6.9
2	5.1	4.8
3	1.9	2.0
4	4.4	4.7
5	3.1	3.6
6	<2.0	.9
7	1.5	1.7
8	<2.0	1.4
9	<2.0	1.5
10	<2.0	.6
11	<2.0	.2
12	<2.0	.7
	8k0	
0	7.3	7.0
1	<.3	.1
2	5.0	4.7
3	<2.0	.3
4	<2.0	1.6
5	<2.0	.2
6	2.5	2.9
7	<2.0	.1
8	<2.0	.6
9	<2.0	1.5
10	<2.0	1.4
11	<2.0	.1
	9k0	
1	<2.0	.1
2	3.2	3.3
3	3.6	4.0
4	2.1	2.4
5	<2.0	1.1
6	<2.0	.7
7	<2.0	.8
8	<2.0	1.8
9	<2.0	1.0
10	<2.0	.6
	10k0	
0	<2.0	.5
1	2.7	3.1
2	<2.0	.2
3	<2.0	1.5
4	<2.0	.2
5	1.8	2.6
6	<2.0	.4
7	1.7	2.3
8	<2.0	1.3
9	<2.0	.8
	11k0	
1	<2.0	1.2
2	<2.0	1.3
3	<2.0	1.3
4	1.7	1.9
5	<2.0	.2
6	<2.0	.9
7	2.5	2.4
	12k0	
0	<2.0	1.4
1	<2.0	.2
2	<2.0	.6
3	<2.0	.8
4	1.8	2.2
5	<2.0	.2
	0k1	
2	15.9	15.3
4	6.3	6.2
6	2.3	2.0
8	3.8	3.6
10	1.4	1.7
12	2.8	2.8
	1k1	
0	9.7	12.1
1	9.0	9.0
2	9.5	8.9
3	2.0	1.2
4	2.8	2.5
5	3.0	2.9
6	6.5	6.1
7	4.5	3.8
8	3.2	3.1
9	2.2	2.1
10	1.0	1.7
11	<1.4	.9
	2k1	
1	16.9	17.3
2	4.6	4.2
3	5.3	5.5
4	3.6	3.5
5	5.4	6.1
6	2.5	2.4
7	6.1	6.9
8	<1.4	.9
9	3.2	3.6
10	<1.4	.7
11	<1.4	.5
12	<1.4	1.0
	3k1	
0	8.3	8.2
1	6.9	6.5
2	5.8	5.8
3	3.3	3.3
4	7.8	7.8
5	5.4	5.9
6	4.4	4.3
7	2.8	2.8
8	2.2	2.3
9	3.2	3.1
10	2.2	2.7
11	1.7	2.1
	4k1	
1	2.0	2.2
2	5.5	5.8
3	1.4	1.7
4	6.2	6.4
5	1.0	1.3
6	5.3	5.8
7	<1.4	.3
8	5.1	5.8
9	<1.4	.3
10	1.4	1.8
	5k1	
0	7.4	7.8
1	5.3	5.4
2	5.2	5.5
3	3.9	3.7
4	1.0	1.6
5	<1.4	1.2
6	5.5	5.6
7	2.5	2.6
8	<1.4	.1
9	1.7	2.5
	6k1	
1	2.7	2.4
2	2.7	2.7
3	5.2	5.1
4	2.0	2.1
5	2.2	2.2
6	1.0	1.3
7	3.3	4.1
8	2.0	2.0
9	1.4	1.6
	7k1	
0	2.8	2.7
1	5.8	6.4
2	3.5	3.7
3	1.0	1.2
4	1.4	1.9
5	2.5	2.9
6	1.4	1.4
7	1.7	2.6
	8k1	
1	<1.4	.6
2	4.6	5.3
3	1.0	1.1
4	3.5	4.2
5	<1.4	1.5
6	<1.4	.5
7	<1.4	1.3
8	2.7	2.9
	9k1	
0	4.8	5.5
1	1.7	1.9
2	<1.4	.6
3	<1.4	.4
4	2.7	.7
5	2.0	3.1
	10k1	
1	<1.4	1.5
2	<1.4	.4
3	2.5	3.0
	11k1	
0	1.0	1.0
1	1.0	1.3
	0k2	
0	22.4	22.9
2	10.5	10.4
4	4.7	4.9
6	6.9	6.4
8	1.8	1.6
10	4.9	4.4
12	3.8	2.9
	1k2	
1	2.5	2.6
2	3.1	3.0
3	5.1	4.7
4	3.5	3.9
5	3.2	3.4
6	3.0	2.8
7	5.1	4.9
8	4.2	3.9
9	2.7	2.5
10	1.2	1.1
	2k2	
0	6.1	6.1
1	3.0	3.3
2	.8	.6
3	3.7	3.5
4	2.7	2.6
5	4.8	4.6
6	2.7	2.4
7	2.1	1.6
8	1.8	2.1
9	2.9	2.7
10	.8	1.0
11	3.9	3.4
	3k2	
1	4.2	4.7
2	3.8	3.7
3	4.7	4.1
4	3.5	3.3
5	3.4	3.2
6	.8	1.1
7	5.1	5.0
8	4.5	4.0
9	.8	1.1
10	.8	.8
	4k2	
0	8.4	7.6
1	3.8	3.6
2	6.9	4.9
3	2.3	2.2
4	3.1	3.1
5	<1.0	.7
6	7.2	6.6
7	2.9	2.7
8	1.4	1.5
9	<1.0	.4
10	2.7	2.3
	5k2	
1	1.4	1.6
2	5.7	5.3
3	3.9	3.7
4	2.7	2.5
5	1.2	1.5
6	.8	1.2
7	1.2	1.2
8	4.1	3.9
9	3.0	2.6
10	1.4	1.6
	6k2	
0	<1.0	.2
1	3.5	3.7
2	.8	1.0
3	<1.0	.8
4	.8	.6
5	5.2	5.2
6	1.4	1.9
7	1.8	1.8
8	.8	.7
9	2.3	2.3
10	.8	.8
	7k2	
1	4.9	5.1
2	2.5	2.0
3	.8	.9
4	1.2	1.5
5	2.2	2.0
6	1.2	1.5
7	2.5	2.4
8	2.1	2.0
9	1.4	1.7
	8k2	
0	3.0	3.4
1	1.2	1.5
2	2.3	2.2
3	.8	.8
4	2.7	2.6
5	.8	1.0
6	2.2	2.2
7	1.2	1.1
	9k2	
1	<1.0	.7
2	3.4	3.2
3	1.4	1.7
4	2.3	2.5
5	.8	.9
6	.8	.6
	10k2	
0	1.8	2.0
1	2.7	2.7
2	1.2	1.0
3	1.4	1.3
	0k3	
2	7.3	6.5
4	3.6	3.2
6	4.3	3.8
8	5.1	4.5
10	2.3	2.0
12	2.1	1.9
	1k3	
0	-	6.8
1	3.0	3.1
2	4.0	3.7
3	2.4	2.4
4	4.0	4.2
5	2.7	2.4
6	6.1	5.9
7	1.7	2.2
8	<1.4	.8
9	2.7	2.6
10	<1.4	1.1
11	1.2	1.5
	2k3	
1	-	9.6
2	3.4	3.7
3	4.8	4.2
4	<1.4	.4
5	4.9	4.9
6	1.7	2.3
7	4.8	4.4
8	<1.4	1.1
9	3.4	3.0
10	<1.4	.9
	3k3	
0	-	7.2
1	-	6.7
2	3.7	3.7
3	<1.4	1.2
4	3.4	3.2
5	4.5	4.5
6	3.4	3.0
7	3.4	3.1
8	1.2	1.9
9	<1.4	.9
10	2.1	2.2
	4k3	
1	1.2	.9
2	5.6	6.2
3	2.1	1.8
4	6.6	6.9
5	<1.4	.7
6	<1.4	.5
7	<1.4	.7
8	3.2	3.0
9	<1.4	.1
10	1.2	1.2
	5k3	
0	5.7	6.9
1	4.9	5.3
2	1.2	2.3
3	<1.4	1.2
4	<1.4	.5
5	1.7	1.6
6	3.4	3.4
7	3.0	2.9
8	<1.4	.5
9	<1.4	.5
10	<1.4	1.6
	6k3	
1	1.7	2.0
2	<1.4	.7
3	4.3	4.2
4	1.2	1.3
5	1.7	1.9
6	<1.4	.7
7	2.1	3.4
8	1.7	1.5
9	1.7	1.6
	7k3	
0	2.7	2.2
1	2.4	2.6
2	2.4	2.6
3	1.7	1.9
4	2.4	2.4
5	2.7	2.7
6	1.2	1.6
7	1.2	1.6
	8k3	
1	<1.4	.2
2	3.0	3.4
3	<1.4	1.0
4	1.7	2.2
5	<1.4	.4
	9k3	
0	3.7	3.5
1	<1.4	1.3
2	<1.4	.2
3	<1.4	.3
4	1.2	1.3
	10k3	
1	1.2	1.4
	0k4	
0	9.9	9.5
2	2.9	3.1
4	3.2	3.3
6	6.8	6.3
8	1.8	1.7
10	3.2	2.3
	0k5	
2	3.5	3.5
4	2.2	2.2
6	2.1	1.8
8	3.8	3.0
10	1.4	1.5
	0k6	
0	5.8	4.5
2	1.3	1.2
4	2.0	1.9
6	4.1	3.0
	0k7	
2	3.7	2.5

were refined with three cycles of the three-dimensional least-squares program of Busing & Levy (1959) with the 441 reflections given in Table 2. Only isotropic temperature factors were used and the hydrogen atoms were not included. The refinement was continued until the shifts in the parameters were less than the estimated errors, at which stage the weighted R index was 0·11. The atomic coordinates given by this refinement (Table 1) were used to calculate the structure factors which are given in Table 2. Fig. 1(a)

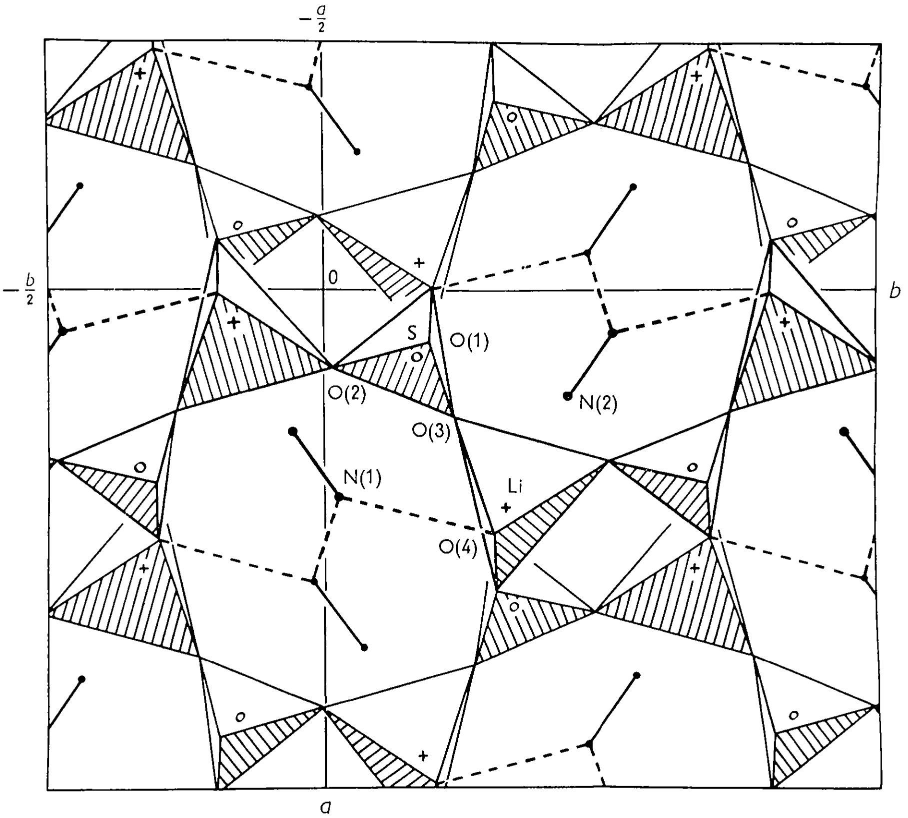

Fig. 2. A view of lithium hydrazinium sulfate projected down the c axis, showing how the hydrazinium ions lie in the channels of the $LiSO_4$ framework. Oxygen atoms are at the apices of the tetrahedra; otherwise atoms are denoted by the same symbols as in Fig. 1.

shows the electron density of the structure projected down the c axis, and Fig. 1(*b*) shows the same after the atoms listed in Table 1 had been removed.

Description of the structure

In crystals of lithium hydrazinium sulfate, the sulfur and lithium atoms are both surrounded by tetrahedra of oxygen atoms. These tetrahedra share corner oxygen atoms to form the three-dimensional network which is shown in Fig. 2. Each oxygen atom is bonded to one lithium atom and to one sulfur atom, so that every LiO_4 tetrahedron is surrounded by four SO_4 tetrahedra and *vice versa.* It is thus possible to trace, in the network, chains of alternating LiO_4 and SO_4 tetrahedra running along the two glide directions and spiraling around the screw axes.

Around half of the screw axes are large channels, which run through the crystal in the direction of the c axis. The hydrazinium ions lie within these channels with their N–N bond axes perpendicular to c. The NH_2 groups of the hydrazinium ions are linked into infinite chains by hydrogen bonds along the screw axes, as shown in Fig. 3(*a*), thus leaving the positively charged $-NH_3$ groups to nestle into cavities in the negatively charged $LiSO_4$ framework.

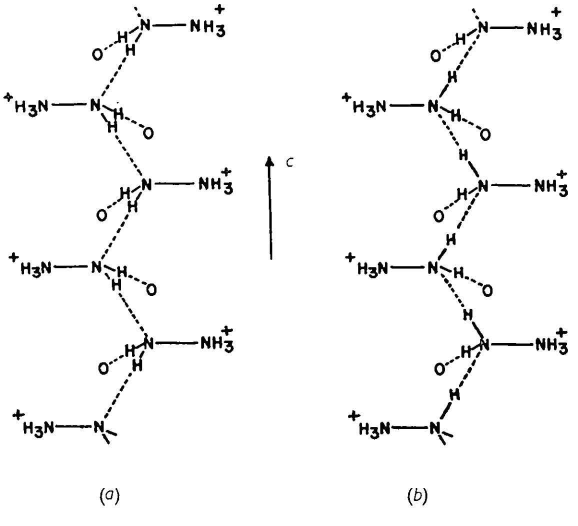

Fig. 3. The arrangement of the hydrogen bonded chain of hydrazinium ions running along the c axis. (*a*) and (*b*) are the two possible configurations that this chain can have if the hydrogen bonds are ordered.

The interatomic distances and angles are given in Table 3, and the distances are shown in Fig. 4. It can be seen that the SO_4 tetrahedron is regular with a mean S–O bond length of 1·475 Å, which agrees well with the value of 1·49 Å found in hydrazonium sulfate by Nitta, Sakurai & Tomiie (1951) and of 1·471 Å found in $Li_2SO_4.H_2O$ by Larsen (1961). The tetrahedron around the lithium atom is, however, slightly distorted, with a standard deviation of the O–Li–O angles of about 8°. The Li–O bonds do not differ significantly from 1·94 Å, which can be compared with the Li–O distance of 1·95 Å found for the tetrahedral lithium in $LiK_2P_3O_9.H_2O$ by Eanes & Ondik (1962). The average angle subtended by the lithium and sulfur atoms at the oxygen is 139° with a standard deviation of 6°.

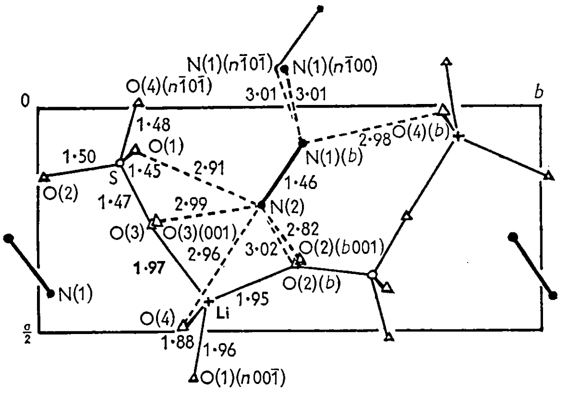

Fig. 4. The structure of lithium hydrazinium sulfate projected down the *c* axis, showing interatomic distances and possible hydrogen bonds (dotted lines). Atomic positions are indicated as in Fig. 1. The labelling of atoms is the same as that used in Tables 1 and 3.

Cuthbert & Petch (1963) have shown by proton magnetic resonance that the hydrazine group exists in this crystal in the form of the hydrazinium ion, $NH_2.NH_3^+$. The distance between the two nitrogen atoms is 1·46 Å, which is the same distance as that found in pure hydrazine by Collin & Lipscomb (1951), and longer than that usually found for the hydrazinium ion (1·45 Å in N_2H_5Cl Sakurai & Tomiie (1952); 1·432 Å in the hydrazine salt of 5-aminotetrazole Bryden (1958)), but the difference is probably not significant.

What is of particular interest is the way in which the hydrazinium ion is hydrogen bonded to its neigh-

Table 3. *Interatomic distances and angles based on the parameters given in Table* 1

The relation between the coordinates of the atoms used in this table and the coordinates of the atoms given in Table 1 is indicated by symmetry operators, *e.g.* O(2)(*b*001) is related to O(2) in Table 1 by a *b* glide followed by a *c* translation of one cell

Environment of the sulfur atom

S = S; O(1) = O(1); O(2) = O(2); O(3) = O(3); O(4) = O(4)($n\bar{1}0\bar{1}$)

S–O(1)	1·45 ± 0·03 Å	O(1)–S–O(2)	110·2 ± 1·0°
S–O(2)	1·50	O(1)–S–O(3)	110·1
S–O(3)	1·47	O(1)–S–O(4)	110·2
S–O(4)	1·48	O(2)–S–O(3)	108·7
		O(2)–S–O(4)	109·3
Mean S–O distance	1·475 Å	O(3)–S–O(4)	108·2
Standard deviation	0·021 Å	Mean O–S–O angle	109·5°
		Standard deviation	0·9°

Environment of the lithium atom

Li = Li; O(1) = O(1)($n00\bar{1}$); O(2) = O(2)(*b*);
O(3) = O(3); O(4) = O(4)

Li–O(1)	1·96 ± 0·04 Å	O(1)–Li–O(2)	118 ± 2°
Li–O(2)	1·95	O(1)–Li–O(3)	114
Li–O(3)	1·97	O(1)–Li–O(4)	110
Li–O(4)	1·88	O(2)–Li–O(3)	98
		O(2)–Li–O(4)	101
Mean Li–O distance	1·940 Å	O(3)–Li–O(4)	114
Standard deviation	0·041 Å	Mean O–Li–O angle	109°
		Standard deviation	8°

Angles at the oxygen atoms

S–O(1)–Li($n\bar{1}00$)	133 ± 2°
S–O(2)–Li($b0\bar{1}0$)	145
S–O(3)–Li	143
S–O(4)($n\bar{1}0\bar{1}$)–Li($n\bar{1}0\bar{1}$)	134
Mean S–O–Li angle	139°
Standard deviation	6°

Hydrazinium ion

N(1) = N(1)(*b*); N(2) = N(2)

N(1)–N(2)	1·46 ± 0·02 Å

Hydrogen bond distances and angles at N(1)

N(2) = N(2); N(1)I = N(1)(*b*); N(1)II = N(1)($n\bar{1}00$);
N(1)III = N(1)($n\bar{1}0\bar{1}$); O(4) = O(4)(*b*)

N(1)I–N(1)II	3·01 ± 0·02 Å
N(1)I–N(1)III	3·01
N(1)I–O(4)	2·98 ± 0·03 Å
N(2)–N(1)I–N(1)II	109·7 ± 1·0°
N(2)–N(1)I–N(1)III	108·3
N(2)–N(1)I–O(4)	135·6
N(1)II–N(1)I–N(1)III	118·6
N(1)II–N(1)I–O(4)	104·1
N(1)III–N(1)I–O(4)	101·9

Hydrogen bond distances and angles at N(2)

N(1) = N(1)(*b*); N(2) = N(2); O(1) = O(1); O(2)I = O(2)(*b*001);
O(2)II–O(2)(*b*); O(3) = O(3)(001); O(4) = O(4)

N(2)–O(1)	2·91 ± 0·03 Å
N(2)–O(2)I	2·82
N(2)–O(2)II	3·02
N(2)–O(3)	2·99
N(2)–O(4)	2·96

Other distances all greater than 3·15 Å

N(1)–N(2)–O(1)	101·3 ± 1·0°
N(1)–N(2)–O(2)I	101·0
N(1)–N(2)–O(2)II	101·7
N(1)–N(2)–O(3)	118·9
N(1)–N(2)–O(4)	165·1

bours (Figs. 3 and 4). Since the hydrogen atoms are not well resolved in this analysis, evidence for the hydrogen bond arrangement is based on the observed short N–N and N–O distances. Thus the short distance of 3·01 Å between the N(1) atoms related by the twofold screw axis suggests that these atoms are hydrogen bonded into chains along the *c* axis. According to this arrangement, a hydrogen atom bonded to one N(1) atom would be pointing at the lone pair of electrons belonging to the next N(1) atom along the chain. The distance of 2·98 Å between N(1) and O(4) suggests that the same nitrogen atom also forms a hydrogen bond to the $LiSO_4$ framework. The N(1) atom thus takes part in three hydrogen bonds, twice as the donor and once as the acceptor of a hydrogen atom. Since it supplies two hydrogen atoms and a lone pair of electrons, it must be part of the NH_2 group of the hydrazinium ion.

Some support for this arrangement is found in the final difference electron density projection (Fig. 1(*b*)) which shows the electron density after all the atoms except hydrogen have been removed. In the regions where the hydrogen atoms are expected, there is a positive electron density of nearly $\frac{1}{2}$ e.Å^{-2}. However, such small amounts of electron density could easily be accounted for by experimental errors, and it would not be wise to base any arguments on their presence or absence.

If the N(1) atom belongs to the NH_2 group, then the N(2) atom must belong to the NH_3^+ group. There are five N(2)–O distances which are short enough to represent hydrogen bonds, but Cuthbert & Petch (1963) have shown that, at room temperature, the NH_3 groups in lithium hydrazinium sulfate are rotating with the N(1)–N(2) bond as the axis of rotation. The smear of electron density in the difference synthesis near N(2) is consistent with this.

Another crystal in which hydrazinium ions are linked by hydrogen bonds is hydrazinium chloride (Sakurai & Tomiie, 1952) where an N–H · · · N distance of 2·95 Å has been found. The arrangement in this case is, however, basically different, since the hydrazinium ions in this crystal are linked end to end to form an infinite spiral around the twofold screw axis.

It remains to comment on one other feature revealed by the difference electron density function, namely, the small anisotropic vibrations which are observed in some of the oxygen atoms. The atoms which were removed from this synthesis were all given isotropic vibrations. It is clear, however, that O(2), O(4), and to a lesser extent O(3), all have small vibrational anisotropies corresponding to a libration of the SO_4 group around the *c* axis.

Discussion

The most interesting feature in the structure of lithium hydrazinium sulfate is the existence of the infinite chains of hydrogen bonds which run through the crystal in the direction of the *c* axis (Fig. 3). The proton magnetic resonance measurements of Cuthbert & Petch (1963) indicate that at room temperature the hydrogen atoms in this chain are in fixed positions, but it is not possible to say which nitrogen atom is the donor and which the acceptor of the hydrogen atom, or indeed whether the hydrogen bonds are ordered. If they are ordered, then there are two possible configurations of the chain which are illustrated at (*a*) and (*b*), Fig. 3. The difference between them is that in one case the hydrogen bonds are pointing in the positive *c* direction, while in the other case they are pointing in the negative *c* direction. A change from one configuration to the other would be accompanied by a change in polarization of the crystal of the same order as that observed during ferroelectric switching. However, since the $LiSO_4$ framework does not have a center of symmetry, such a change would result in a crystallographically distinct structure, unless the framework simultaneously switched from a right to a left handed form.

There are two mechanisms which could produce a change in the configuration of the chain; one is the rotation of the NH_2 groups, the other a transfer of the proton along the hydrogen bond from one nitrogen atom to the next. A combination of both effects would allow protons to migrate along the chain, and this could explain the large electrical conductivity which occurs along the *c* axis. Further work is in progress in this laboratory to test various hypotheses which might explain the interesting electrical properties of this substance.

I wish to acknowledge the help of J. D. Cuthbert and H. E. Petch in suggesting this problem, supplying crystals, and in discussion; W. R. Busing and H. A. Levy for the use of their least squares program; The Institute of Computer Science, Toronto, for the use of their IBM 7090 Computer; and the National Research Council of Canada for supporting this work.

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The Crystal Structure of Ferroelectric Lithium Hydrazinium Sulfate*

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(*Received* 31 *May* 1963 *and in revised form* 8 *August* 1963)

The crystal structure of lithium hydrazinium sulfate has been determined by the heavy atom method from $0kl$, $h0l$ and $hk0$ data. Bond lengths and angles based on three-dimensional data are given, e.s.d. 0·008 Å and 1°.

The N–N distance found is 1·447 Å, which corresponds to previously reported values for the $N_2H_5^+$ ion. The nitrogen atoms form in the direction of the c axis an infinite hydrogen-bonded zigzag chain of the type NH–N with a distance of 3·018 Å. The length of one of the S–O bonds is 1·557 Å, which is considerably longer than the normally accepted value for that ion. That of another bond is 1·430 Å, which indicates a large amount of double bond character.

The structure is held together by three-dimensional network of weak hydrogen bonds. Tentative positions of the hydrogen atoms are assigned.

Introduction

The preceding article (Brown, 1964) concerns the crystal structure of the ferroelectric lithium hydrazinium sulfate.

This paper represents an independent structure analysis of the same compound, which was carried out concurrently. However, after it was submitted for publication, the work of Brown was pointed out to us by one of the editors, and Dr. Brown was so courteous as to provide us with a copy of his manuscript. In order to avoid duplication, a large amount of material has been omitted from this publication.

The intensity data

The intensities were recorded with both a Weissenberg camera and a General Electric XRD 5 diffractometer equipped with a single-crystal orienter, Cu $K\alpha$ radiation being used. To reduce the background and the accidental overlapping of β reflections and harmonics, a nickel filter and pulse-height analyzer were employed. The crystal used for data collection was carefully ground into a cylinder with a radius of 0·015 cm and with the axis coinciding with the c axis. For the $h0l$ projection 30 reflections were observed, and 2 had zero magnitude. For the $0kl$ and $hk0$ projections these numbers are respectively 30 and 0, 83 and 16. The data were not corrected for absorption but the usual corrections for the Lorentz and polarization factors were applied. In a later stage of the structure determination a complete set of three-dimensional data was obtained. Fifty-three of the 505 possible reflections, for which $\sin\theta$ is smaller than 0·9659 ($2\theta < 150°$), had a magnitude smaller than detectable. In all cases the intensities were measured with the counter and the specimen rotating in the ratio 2 to 1.

Structure determination

The x and y coordinates of the sulfur atoms were determined from the Patterson function $P(u,v)$ from which the peak at the origin was removed. The approximate positions of the oxygen atoms were obtained from a subsequent Fourier synthesis based on the signs as determined by the sulfur atoms alone. After the sulfur and oxygen atoms had been included in the structure factor calculations, the discrepancy index R for this projection was 0·25. Two additional Fourier syntheses revealed the positions of the nitrogen atoms and provided improved positional

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* Work performed partly under the auspices of the U.S. Atomic Energy Commission.

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