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The Crystal Structure of Lithium Sodium Sulfate*

BY B. MOROSIN AND D. L. SMITH†

Sandia Laboratory, Albuquerque, New Mexico 87115, *U.S.A.*

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The crystal structure of $LiNaSO_4$ has been determined by three-dimensional Fourier methods and refined by full-matrix least-squares procedures. The space group is $P31c$ with cell dimensions $a_0 = 7{\cdot}6270$, $c_0 = 9{\cdot}8579$ Å. Three crystallographically different sulfate groups are situated on two different threefold axes. The lithium and sodium ions are surrounded by irregular arrangements of four and eight oxygen atoms, respectively.

Introduction

In the course of studying the phase diagram of the Li_2SO_4–Na_2SO_4–H_2O system, Cavalca & Nardelli (1952) isolated and reported the space group and lattice constants for $LiNaSO_4$. They pointed out that this compound is not isomorphous with $LiKSO_4$. A compound containing both sodium and lithium ions was considered of interest to complement nuclear magnetic resonance studies in our laboratory (Anderson, 1961). Therefore, the current structure determination of $LiNaSO_4$ was undertaken to establish positional parameters and nearest neighbors of the alkaline metal ions.

Experimental

Lattice constants for $LiNaSO_4$ ($a_0 = 7{\cdot}6270(7)$ and $c_0 = 9{\cdot}8579(10)$ Å) were obtained with Cu $K\alpha$ radiation (λ for $K\alpha_1 = 1{\cdot}54050$ Å) by least-squares fit of high 2θ values measured on films taken with a 115 mm diameter Weissenberg camera which accepts Straumanis film loading. Systematic absences of $hh\overline{2h}l$ for l odd and evidence of a piezoelectric effect indicate the space group is $P31c$. Cavalca & Nardelli reported an experimental density of 2·536 g.cm^{-3} compared with 2·527 g.cm^{-3} calculated from the above lattice constants and six molecular weights of $LiNaSO_4$ per cell. No evidence of ferroelectricity was found in this noncentrosymmetric compound.

Three-dimensional Mo $K\alpha$ intensity data were measured using balanced filters with a Picker diffractometer equipped with a General Electric single-crystal orienter and scintillation counter. A unique set of 496 reflections (27 were considered unobserved) was obtained by averaging symmetry-equivalent reflections. No absorption corrections were necessary for the spherically ground crystal ($\mu R = 0{\cdot}5$).

Lorentz and polarization factors were applied and structure factors calculated using both neutral and charged (extrapolated) scattering factors from Table 3.3.1A of *International Tables for X-ray Crystallography* (1962, p. 202) (denoted hereafter ITXC).

Structure determination

A three-dimensional Patterson function was calculated, and the sulfur–sulfur vectors were found to be consistent with sulfate groups situated on the threefold axes (special positions (*a*) and (*b*) in space group $P31c$) rather than in general positions. Succeeding Fourier syntheses resolved the sodium ion and oxygen atoms for the final structure as well as weaker oxygen 'ghosts' corresponding to sulfate ions oriented in the opposite direction. Full-matrix least-squares refinement of positional and isotropic thermal parameters was attempted for several models differing only in the arrangements of oxygen atoms. The 'ghost' peaks vanished and the oxygen thermal parameters successfully converged only

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† Present address: Kodak Research Laboratory, Rochester, New York 14650, U.S.A.

for the structure reported here. A Fourier synthesis of this succcessful model contained a large spherical peak which was interpreted to be the lithium ion. Refinement was continued using anisotropic thermal factors with both neutral and charged scattering factors. The function $\Sigma\, w(F_o-F_c)^2$ was minimized; unit and zero weights were used for observed and unobserved reflections, respectively. The final atomic positional and anisotropic thermal parameters (Table 1) and the list of observed and calculated structure factors (Table 2) were obtained using neutral scattering factors. The reliability index, R, is 0·060 for this refinement. The average and maximum parameter shifts as parts of the estimated standard deviations, $(s/\text{e.s.d.})_{\text{ave}}$ and $(s/\text{e.s.d.})_{\text{max}}$, are 0·051 and 0·22 (for B_{12} of the O(4) atom), respectively. Final Fourier and difference syntheses verified the correctness of the structure. The thermal factors for S(1) and O(2) are non-positive definite. The parallel refinement ($R=0{\cdot}062$; $(s/\text{e.s.d.})_{\text{ave}}=0{\cdot}057$ and $(s/\text{e.s.d.})_{\text{max}}=0{\cdot}23$ for B_{12} of the O(4) atom) using charged scattering factors (S^{6+}, O^{2-}, Na^+ and Li^+) resulted in atomic positional parameters which differ from those in Table 1 by a maximum of $1{\cdot}8\sigma$ for the z parameter of O(5) and in thermal factors for the sulfur atoms which are about 4σ higher. For this parallel refinement, the thermal parameter, B_{33}, for O(2) is again negative with the value of $-0{\cdot}35$ Å^2. These negative values are not significantly different from zero when the estimated standard deviations are considered. Projections along the c_0 and a_0 axes are given in Fig. 1.

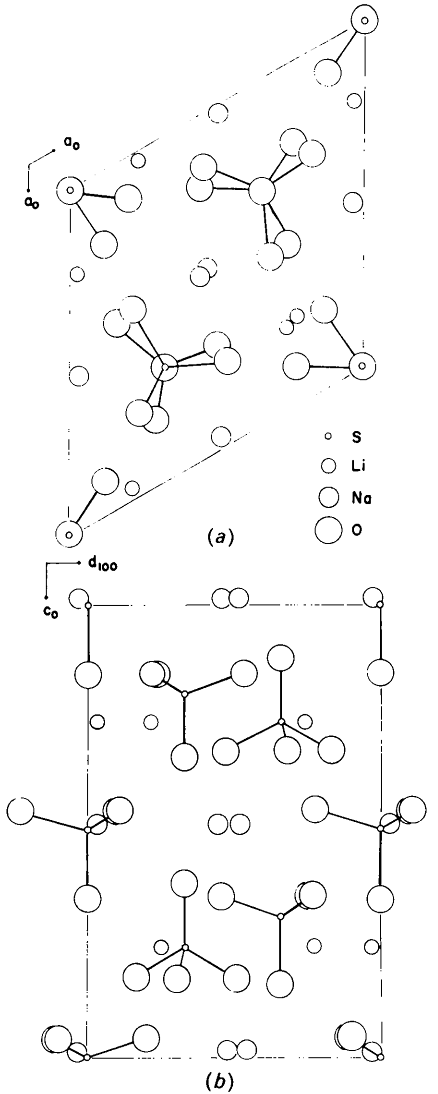

Fig. 1. (*a*) A representation of the crystal structure of $LiNaSO_4$ viewed along the c axis. Solid lines connecting sulfur and oxygen atoms are between atoms contained within $z=0{\cdot}0$ to 1·0. (*b*) Viewed along the a axis. Atoms along threefold axes which were hidden in (*a*) can now be seen. Again partly hidden or connected atoms are contained within $y=$ 0·0 to 1·0.

Discussion

The average S–O separation (1·469 Å) found in $LiNaSO_4$ is in agreement with similar values (1·467–1·474 Å) found in other sulfates (ITCX, Table 4.1.9, p. 272; for more recent values see Larson, 1965). The trend in the spread* of values for S–O separations

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* The spread of values decreases slightly when thermal motion is considered. Values for S–O separations, calculated by the assumption of in-phase motion (Busing & Levy, 1964), are 1·510, 1·487, 1·466, 1·499, 1·467 and 1·483 Å for the S(1)–O(1), S(1)–O(4), S(2)–O(2), S(2)–O(5), S(3)–O(3), and S(3)–O(6) bond lengths, respectively.

Table 1. *Atomic positional and anisotropic thermal parameters for* $LiNaSO_4$

z parameter for S(1) arbitrarily set to zero; $B_{11}=B_{22}=2B_{12}$ for atoms on threefold axes; thermal parameters of the form

$$\exp\left(-\tfrac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3}B_{ij}h_ih_ja_i^*a_i^*\right).$$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Li	0·0308 (27)	0·2503 (27)	0·2583 (17)	2·17 (67)	1·63 (64)	1·30 (58)	1·10 (57)	−0·21 (35)	0·05 (50)
Na	0·02517 (6)	0·5468 (6)	0·4881 (6)	1·27 (14)	1·70 (16)	1·64 (14)	0·41 (14)	−0·10 (11)	−0·14 (16)
S(1)	0	0	0	0·62 (7)		−0·23 (9)			
S(2)	$\frac{1}{3}$	$\frac{2}{3}$	0·1976 (7)	0·40 (8)		0·39 (11)			
S(3)	$\frac{2}{3}$	$\frac{1}{3}$	0·2632 (7)	0·57 (8)		0·26 (10)			
O(1)	0	0	0·1528 (11)	1·06 (29)		0·90 (38)			
O(2)	$\frac{1}{3}$	$\frac{2}{3}$	0·3449 (11)	1·92 (34)		−0·41 (37)			
O(3)	$\frac{2}{3}$	$\frac{1}{3}$	0·1168 (16)	3·20 (51)		1·35 (60)			
O(4)	0·2125 (9)	0·1108 (11)	−0·0460 (7)	1·06 (20)	2·14 (27)	0·70 (25)	0·93 (22)	0·65 (11)	0·40 (20)
O(5)	0·2218 (12)	0·4557 (10)	0·1468 (8)	2·20 (31)	0·46 (21)	1·40 (28)	−0·08 (21)	−0·07 (15)	−0·28 (19)
O(6)	0·4776 (12)	0·1697 (16)	0·3166 (10)	1·28 (29)	3·29 (25)	2·87 (33)	0·22 (27)	0·29 (10)	0·83 (31)

Table 2. *Observed and calculated structure factors*

An asterisk designates 'less than'.

L	10FO	10FC	10A	10B
	H =	0	K =	0
2	120	114	111	23
4	700	665	546	-380
6	989	973	720	-654
8	340	342	311	-141
10	170	160	17	-159
12	159	167	162	38
0	104	98	-98	0
1	117	82	-11	81
2	532	519	517	-48
3	506	507	-179	-474
4	252	255	131	-219
5	380	384	227	309
6	69	86	18	-84
7	299	298	-238	-179
8	85	69	53	44
9	60	71	58	41
10*	36	18	-4	18
11	63	66	-61	-24
12	75	88	74	-47
13	99	89	89	-2
	H =	1	K =	1
0	914	970	970	34
2	403	349	-344	-58
4	210	185	-128	-134
6	156	137	131	-39
8	82	53	49	-22
10	73	65	31	-58
12	226	217	85	199
	H =	2	K =	0
0	243	233	233	0
1	132	123	-121	-21
2	861	853	850	-65
3	254	235	-121	-202
4	467	480	470	-97
5	361	350	-249	-246
6	453	464	455	-94
7	372	370	202	309
8	308	298	291	-63
9	269	273	-261	-82
10	245	264	256	-63
11	126	121	108	56
12	252	260	193	-174
13	52	71	-38	60
	H =	2	K =	1
0	89	82	-8	81
1	230	206	-206	-16
2	291	311	25	310
3	69	59	53	25
4	285	265	-144	223
5	225	211	-1	211
6	313	301	299	-37
7	338	316	-305	-82
8	308	303	118	280
9	249	247	197	148
10	159	162	128	98
11	103	106	-94	49
12	181	187	141	-123
13	101	93	89	29
	H =	2	K =	-1
2	593	668	-431	509
4	163	127	125	20
6	180	171	124	117
8	175	174	158	74
10	102	103	101	20
12	232	235	123	199
	H =	2	K =	2
0	872	895	869	214
2	306	269	268	22
4	429	372	309	-207
6	381	366	357	79
8	341	328	304	-122
10	236	216	159	-146
12	227	233	190	134
	H =	3	K =	0
0	366	372	372	-0
1	489	530	15	-530
2	365	357	-302	191
3	78	77	-76	12
4	194	178	177	18
5	353	360	-335	-131
6	207	200	30	197
7	184	181	-146	-106
8	185	191	189	26
9	83	92	-4	92
10	166	170	156	-68
11	85	102	-55	87
12	253	255	144	210
13*	44	19	-19	5
	H =	3	K =	1
0	356	379	-263	-273
1	105	59	2	-59
2	163	147	75	-126
3	198	200	-176	-95
4	87	49	26	-42
5	221	201	-121	-160
6	154	91	5	-91
7	362	350	196	290
8	98	62	50	37
9	249	237	-231	-55
10	80	79	79	-7
11	137	142	129	59
12	114	124	76	-97
	H =	3	K =	-1
1	264	251	13	-251
2	201	150	85	124
3	149	156	-133	81
4	276	277	-266	-78
5	320	322	194	257
6	293	277	276	-23
7	363	362	-284	-225
8	125	122	94	77
9	266	269	172	207
10	115	97	29	92
11	64	47	-45	15
12	207	234	142	-186
13	77	73	73	2
	H =	3	K =	2
0	61	52	45	25
1	124	109	-78	-76
2	323	309	300	73
3	259	237	-5	-237
4	84	92	91	-11
5	201	177	165	66
6	191	185	183	-28
7	314	297	-255	-153
8	93	100	97	23
9	136	137	136	17
10	74	85	65	55
11	107	101	-85	-53
12	116	133	93	-95
	H =	3	K =	3
0	712	751	716	-228
2	194	173	-154	79
4	384	401	58	-397
6	208	200	72	-186
8	76	63	31	-55
10	127	131	-95	-91
	H =	4	K =	0
0	426	414	414	0
1	137	135	-12	-135
2	341	355	330	130
3	239	227	-135	-182
4	185	170	169	-25
5	223	207	47	201
6	414	413	388	-142
7	311	311	-263	-166
8	315	312	301	80
9	166	175	114	133
10	100	111	111	-9
11	78	77	-70	31
12	254	273	198	-188
	H =	4	K =	1
0	614	647	630	150
1	65	44	-44	3
2	340	334	-240	232
3	188	192	-106	161
4	221	201	192	60
5	79	77	-17	75
6	180	187	147	116
7	70	75	-30	69
8	163	174	161	66
9	81	80	27	76
10	105	100	98	-16
11	52	53	18	50
12	206	215	138	165
	H =	4	K =	-1
1	175	176	-114	134
2	260	264	210	161
3	224	204	-56	-196
4	205	216	35	213
5	285	299	-254	-137
6	257	265	169	203
7	371	381	185	333
8	217	204	160	128
9	247	245	-235	-68
10	178	161	133	91
11	120	113	96	60
12	152	176	170	-48
	H =	4	K =	2
0	178	173	170	-31
1	80	58	43	-39
2	408	447	446	-22
3	176	177	85	156
4	221	215	200	-80
5	267	259	-184	-183
6	244	256	225	-122
7	215	215	171	131
8	115	134	127	-44
9	104	107	-66	-83
10	85	92	92	-6
11*	44	49	42	26
	H =	4	K =	-2
2	315	310	74	301
4	601	597	568	-184
6	283	244	236	-61
8	356	315	312	-46
10	279	282	225	-170
12	170	170	135	104
	H =	4	K =	3
0	129	127	27	124
1	147	147	-109	98
2	338	332	329	-43
3	146	145	-142	-28
4	99	72	72	-2
5	292	290	175	231
6	161	150	150	-7
7	209	210	-200	-62
8	48	61	61	-3
9	160	165	97	133
10	54	58	45	37
	H =	4	K =	4
0	467	468	466	-36
2	138	142	-105	96
4	241	247	226	-100
6	92	62	61	-10
8	146	120	114	38
	H =	5	K =	0
0*	29	23	-23	-0
1	135	116	-73	-90
2	244	235	203	118
3	84	90	61	67
4	33	35	25	-25
5	327	306	-111	-285
6	164	159	159	-14
7	206	203	154	133
8	200	200	174	98
9	169	178	-131	-121
10*	41	62	60	16
11	77	73	59	-42
	H =	5	K =	1
0	202	188	-178	-62
1	159	159	116	108
2	267	264	219	-147
3	52	55	55	1
4	106	100	-28	-96
5	293	282	169	226
6	91	76	70	-30
7	199	185	-64	-174
8	65	60	52	-30
9	180	198	191	50
10	56	42	39	-15
11	61	59	-54	-23
	H =	5	K =	-1
1	97	104	68	79
2	314	309	-308	-28
3	127	113	106	40
4	190	188	144	-120
5	63	59	33	49
6	124	100	55	-83
7	44	29	27	9
8	75	71	71	-11
9	67	70	64	28
10	97	102	48	-90
11*	43	31	30	5
12	161	151	74	132
	H =	5	K =	2
0	496	509	509	16
1	83	85	74	-41
2	162	159	-103	121
3	109	112	-37	-106
4	216	206	203	-33
5	74	79	70	-38
6	133	132	131	-14
7	114	77	25	-73
8	115	114	109	33
9	56	51	-33	-39
10	100	110	96	-52
	H =	5	K =	-2
1	153	159	-94	-128
2	319	339	307	-144
3	283	302	-199	-226
4	73	69	22	-65
5	215	211	156	142
6	197	220	163	-148
7	339	360	-290	-214
8	53	45	45	-7
9	111	110	60	93
10	41	40	40	-2
11	91	96	-85	-44
12	98	111	55	-96
	H =	5	K =	3
0	87	95	-11	-94
1	40	23	3	23
2	179	169	120	-119
3	50	50	45	22
4	64	26	-17	-20
5	158	160	-111	-116
6	120	119	68	-97
7	192	187	124	140
8	53	28	27	7
9	121	131	-116	-59
	H =	5	K =	4
0	51	36	36	4
1	77	72	31	-65
2	159	164	147	74
3	121	121	16	-120
4*	41	25	8	24
5	102	102	76	68
6	142	135	135	-11
7	201	211	-132	-164
	H =	5	K =	5
0	249	242	241	-23
2	128	125	-124	-19
4	119	135	116	-69
	H =	6	K =	0
0	507	507	507	-0
1	136	130	-65	113
2	117	115	-113	24
3	87	81	50	-63
4	248	239	238	22
5	118	112	110	-18
6	197	188	181	51
7	76	66	64	18
8	121	124	123	-20
9	108	102	-40	-94
10	176	180	173	-48
	H =	6	K =	1
0	102	93	-0	93
1	142	130	-84	99
2	234	239	164	174
3	211	203	73	190
4	117	106	-22	104
5	141	130	-89	-95
6	205	211	211	-2
7	253	237	155	179
8	189	201	142	142
9	112	120	-97	-70
	H =	6	K =	-1
1	144	136	57	123
2	278	274	215	170
3	33	16	-15	-7
4	155	148	80	124
5	280	275	112	251
6	143	131	88	97
7	211	200	-102	-172
8	169	171	132	108
9	159	167	148	78
10	115	147	124	78
11	73	78	-77	-6
	H =	6	K =	2
0	64	49	18	46
1	52	36	-8	-35
2	191	196	193	35
3	90	99	-28	-95
4*	39	27	24	11
5	119	101	61	81
6	151	173	172	-15
7	228	228	-170	-152
8	131	141	126	63
	H =	6	K =	-2
1	131	148	115	-94
2	416	460	449	-98
3	160	156	11	156
4	193	189	161	-99
5	237	218	-128	-176
6	251	261	235	-114
7	176	176	165	59
8	107	119	113	-38
9	103	109	-100	-45
10	67	78	75	-22
11	49	48	47	8
	H =	6	K =	3
0	264	280	276	48
1	59	25	-19	-16
2	127	126	-90	89
3	58	72	-64	33
4	170	172	171	-4
5	138	143	-130	59
6	117	134	71	113
7	45	45	-40	20
	H =	6	K =	-3
2	270	272	-63	264
4	120	106	68	-81
6	225	213	213	-13
8	136	131	98	87
10*	42	14	-10	-9
	H =	6	K =	4
0	44	41	-40	-6
1	82	70	-45	-54
2	132	132	132	8
3*	44	38	-36	12
4	54	47	16	44
	H =	7	K =	0
0	39	39	-39	-0
1	51	41	33	-24
2	212	207	206	8
3	69	60	41	-43
4	78	67	55	37
5	125	116	66	95
6	156	152	152	-1
7	236	240	-103	-217
8	94	117	114	30
9	134	132	131	14
	H =	7	K =	1
0	297	299	294	-56
1	52	53	47	24
2	137	110	-110	6
3	62	59	45	38
4	159	167	136	-97
5	56	51	51	-6
6	81	48	42	22
7*	43	32	32	-0
8	90	85	76	-37
	H =	7	K =	-1
1	113	100	64	77
2	170	143	142	12
3	217	218	130	175
4	120	126	-96	-82
5	138	128	14	-127
6	173	162	151	-61
7	253	265	238	117
8	128	99	90	41
9	103	112	-73	-86
	H =	7	K =	2
0*	41	6	-1	6
1	96	105	35	-99
2	176	164	164	-0
3	57	36	-14	-33
4	88	90	82	37
5	162	162	-59	-151
6	126	121	121	-5
	H =	7	K =	-2
1	51	52	-50	-14
2	120	101	-91	44
3	115	104	-22	-101
4	194	200	135	-147
5	67	54	-27	-47
6	131	126	124	24
7	53	45	-45	4
8	105	101	94	-37
9	67	71	-37	-61
10	63	61	42	-44
	H =	7	K =	3
0	75	70	3	-70
1*	43	26	-25	10
2	113	109	100	44
3	82	80	-34	-73
4*	45	32	-20	-26
	H =	7	K =	-3
1	148	143	3	142
2	303	280	263	-98
3	114	95	56	-77
4	145	145	111	-93
5	273	265	223	143
6	131	158	68	-143
7	160	134	-121	-59
8*	40	40	26	-31
9	160	168	161	47
10*	44	41	39	-10
	H =	8	K =	0
0*	40	19	19	-0
1	55	55	40	-38
2	187	183	182	-5
3*	41	13	11	6
4*	42	55	55	3
5	163	161	-102	-124
6	111	115	107	-41
7	153	147	129	70
	H =	8	K =	1
0	73	73	69	21
1	68	85	-62	58
2	147	149	145	33
3	71	82	-70	-44
4	71	62	50	37
5	142	134	77	110
	H =	8	K =	-1
1	76	79	-45	65
2	189	188	-125	141
3	55	43	-10	42
4	206	183	183	-8
5*	41	44	-15	42
6	129	134	65	117
7	75	32	1	32
8	128	121	110	51
	H =	8	K =	2
0	265	279	279	1
1	72	71	8	-70
2	32	98	-70	68
	H =	8	K =	-2
1	71	70	-19	-67
2	182	186	178	56
3	84	83	-47	-69
4*	39	31	31	2
5	118	117	74	91
6	151	144	140	-34
7	230	234	-184	-144
8	122	131	118	57
	H =	8	K =	-3
1	59	58	10	-57
2	173	166	144	81
3	77	91	-43	81
4	119	118	40	111
5	157	152	-90	-122
6	142	142	135	44
7	177	177	107	141
8	106	122	92	80
9	135	146	-139	-47
	H =	8	K =	-4
2	101	81	-39	72
4	228	219	185	-116
6	96	109	106	27
8	135	142	140	-23
	H =	9	K =	0
0	385	389	389	-0
1	46	44	-13	-42
2	77	80	-28	74
3*	44	10	3	9
	H =	9	K =	-1
1	57	55	-1	55
2	157	161	145	-70
3	67	71	-6	-71
4*	44	19	10	-16
5	181	203	148	139
	H =	9	K =	-2
1	73	61	-54	-27
2	175	187	180	-48
3	64	61	-48	-37
4	74	63	48	41
5	179	183	-142	-115
6	115	116	113	-27
	H =	9	K =	-3
1	103	103	93	-45
2	128	119	-116	29
3	45	45	32	32
4	182	188	177	-62
5	80	37	-36	11
6	74	52	35	38
7*	44	23	23	-6
	H =	9	K =	-4
1	94	95	-64	-70
2	158	151	148	27
3	121	123	-102	-70
4*	41	14	13	-7
5	83	75	3	75
6	154	158	150	-50
7	220	222	-189	-117
	H =	10	K =	-2
1	62	58	11	-57
2	101	117	-95	69
	H =	10	K =	-3
1*	43	44	-44	-6
2	141	148	131	70
3	92	93	-63	-67
4	65	55	-42	36
	H =	10	K =	-4
1	81	77	-66	-39
2	127	131	131	-8
3*	44	23	23	-4
4	51	47	19	43
	H =	10	K =	-5
2	146	142	-106	94
4	167	170	164	44

(Table 3) may be reconciled by consideration of the nearest neighbor environment of the particular oxygen atoms involved. For the shorter separations, the S(2)–O(2) and S(3′)–O(3′) bonds lie on a threefold axis with a 2·680 Å contact between the O(2) and O(3′) atoms while the S(3)–O(6) bond points into the junction of three polyhedra about the alkaline metal ions which involve ionic separations among the shortest in the crystal structure. In contrast the longest separation, S(1)–O(1), involves an oxygen atom whose nearest oxygen neighbor (intersulfate) is 3·01 Å and whose nearest cation (lithium) is 2·08 Å. These separations are among the largest separations of their type in the crystal. The interatomic separations found in $LiNaSO_4$ may be compared with the 2·64–2·77 Å intersulfate contacts in $CuSO_4$ and $ZnSO_4$ (Kokkoros & Rentzeperis, 1958), $K_2Mg_2(SO_4)_3$ (Zemann & Zemann, 1957), and $KFe(SO_4)_2H_2O$ (Graeber, Morosin & Rosenzweig, 1965), the 1·86–2·0 Å Li–O separations found with fourfold coordination about lithium (ITXC, Table 4.1.1, p. 258; Larson, 1965) and the 2·34–2·80 Å Na–O separations found with sevenfold coordination about sodium (ITXC; Cocco, Corazza & Sabelli, 1965).

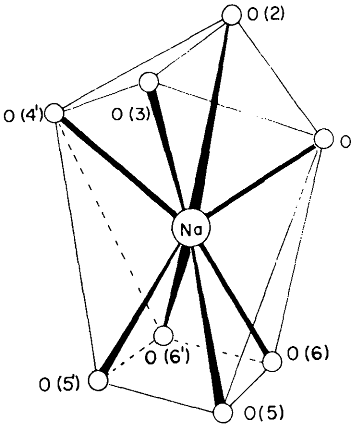

Fig. 2. Idealized coordination about the sodium ion suggests a distorted Archimedean antiprism with the O(4) type oxygen atoms displaced downwards from the ideal plane. Oxygen atoms O(3) and O(2) lie on a threefold axis so that the O(2), O(3), O(4) face is shared with a similar adjacent sodium polyhedron. The edges O(5)–O(5′) and O(6)–O(6′) are intrasulfate separations.

The polyhedra formed by oxygen atoms about the alkaline metal ions are not regular. The distorted tetrahedron about the lithium ion appears to be shortened along one of the three twofold axes of the tetrahedron. The polyhedron about the sodium ion is more complex, resembling a distorted Archimedean antiprism. If only the six closest neighbors are considered (as a distorted

Table 3. *Interatomic separations and angles in* $LiNaSO_4$

Sulfate groups			
S(1)–O(1)	1·506 Å	O(1)–S(1)–O(4)	107·9°
S(1)–O(4)	1·476	O(4)–S(1)–O(4′)	111·0
S(2)–O(2)	1·453	O(2)–S(2)–O(5)	109·2
S(2)–O(5)	1·482	O(5)–S(2)–O(5′)	109·8
S(3)–O(3)	1·454	O(3)–S(3)–O(6)	107·7
S(3)–O(6)	1·444	O(6)–S(3)–O(6′)	111·2
Distorted tetrahedron about the lithium ion			
Li–O(5)	1·872 Å	O(6′)–Li–O(4′)	94·5°
Li–O(6′)	1·881	O(1) –Li–O(5)	99·1
Li–O(1)	2·082	O(1) –Li–O(4′)	104·0
Li–O(4)	2·087	O(6′)–Li–O(5)	111·6
O(4′)–O(6′)	2·916	O(4′)–Li–O(5)	120·0
O(1) –O(5)	3·011	O(1) –Li–O(6′)	129·4
O(5) –O(6′)	3·103		
O(4′)–O(5)	3·217		
O(4′)–O(1)	3·286		
O(1) –O(6′)	3·584		
Sodium nearest neighbors:			
Na–O(6)	2·383 Å	Na–O(5′)	2·512 Å
Na–O(4)	2·398	Na–O(5)	2·683
Na–O(3)	2·414	Na–O(4′)	2·951
Na–O(2)	2·491	Na–O(6′)	2·979
Oxygen in sodium polyhedron:			
O(6) –O(6′)	2·348 Å	O(5)–O(6)	3·293 Å
O(5) –O(5′)	2·416	O(4)–O(5)	3·430
O(2) –O(3)	2·680	O(4)–O(3)	3·402
O(4) –O(6)	2·916	O(2)–O(6)	3·434
O(2) –O(4)	3·187	O(2)–O(6′)	4·454
O(4′)–O(5′)	3·238	O(3)–O(5)	3·865
O(4′)–O(6′)	3·269	O(3)–O(5)	3·955

Next closest oxygen to the lithium and sodium ions are 2·97 and 3·55 Å, respectively. The average standard deviations for the S–O, Li–O, O–O, Na–O bond separations are 0·015, 0·036, 0·019 and 0·015 Å, respectively, and those for the O–S–O and O–Li–O bond angles are 0·7 and 1·2°, respectively.

octahedral arrangement of oxygen atoms), the O–Na–O angles vary from 55 to 140° with the smallest angle involving oxygen atoms which share an edge with the sulfate tetrahedron. The next smallest angle (66°) involves the oxygen atoms forming the smallest intersulfate separation mentioned above; hence, this edge is shared by three identical, but rotated, polyhedra. However, such an octahedral environment appears to be too restrictive for the coordination about the sodium ion. By considering the next two closest oxygen atoms [O(6′) and O(4′)] in the coordination sphere, a distorted Archimedean antiprism (Fig. 2) is obtained. In this idealized polyhedron, the O(4) type oxygen atoms are displaced toward the sodium ion from the top plane of that required for a regular antiprism. The calcium ion in $CaNa_2(SO_4)_2$ (Cocco, Corazza & Sabelli, 1965) is also situated in a distorted antiprism consisting of six closer (2·36–2·47 Å) and two more distant (2·74 Å) oxygen atoms.

Lithium sodium sulfate belongs to a class of compounds of the form $M'M''XO_4$ which are all trigonal or higher in symmetry, but belong to different space groups, and which have lattice constants related by simple multiples. Among these compounds are: (1) $LiNaSO_4$ in space group $P31c$; (2) $KLiSO_4$ and $KAlSiO_4$ in space group $P6_32$ (Claringbull & Bannister (1948) showed these to be related to hexagonal tridymite, nepheline and kaliophilite); (3) $NaK_3(SO_4)_2$ and $NaKSO_4$ in space group $P\bar{3}m1$ (Bellanca, 1943); (4) anhydrous alums such as $KAl(SO_4)_2$ in space group $P321$ (Vegard & Maurstad, 1929); and (5) silicates such as $NaAlSiO_4$ and $KLaSiO_4$ in space group $P6_3$ (subcell to $KLiSO_4$; Eitel, Herlinger & Trömel, 1930). With the exception of the last set of silicates, for which the detailed crystal structure has not been proposed, all these compounds have sulfate or silicate groups situated on the threefold axes. The relative locations of the XO_4 groups appear to be governed by the manner in which the metal ions form their coordination polyhedra.

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The Crystal Structure of L-Leucine Hydrobromide*

By E. Subramanian†

Centre of Advanced Study in Physics, University of Madras, Madras 25, India

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The crystal structure of L-leucine hydrobromide has been determined. The orthorhombic unit cell has the dimensions $a=7{\cdot}29$, $b=24{\cdot}51$, $c=5{\cdot}54$ Å and the space group is $P2_12_12_1$. There are four molecules of $C_6H_{14}NO_2^+.Br^-$ in the cell. The trial structure, obtained by a combination of the 'heavy atom' method and the method of structure invariants applied to the c-axis projection, has been refined by three-dimensional least-squares method to an R value of 0·11. All available hydrogen atoms are involved in hydrogen bonding.

Introduction

The investigation of the crystal structure of leucine was taken up as part of a program of research work in this department on the structure analysis of amino acids and proteins. Leucine is among the most important amino acids essential for the growth and maintenance of living organisms, and, while the crystal structures of most of the amino acids have been determined, the structure analysis of leucine has not so far been reported except as an N-terminal residue in the tripeptide leucylprolylglycine (Leung & Marsh, 1958). Knowledge of the stereochemistry of leucine as a structural unit in proteins would be of great value and consequently the structure analysis was taken up.

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* Contribution No. 198 from The Centre of Advanced Study in Physics, University of Madras, Madras 25, India.

† Present address: Department of Chemistry, Gates and Crellin Laboratories, California Institute of Technology, Pasadena, California 91109, U.S.A. This work was supported in part by a Public Health Service Research Grant no. HE 02143 from the National Heart Institute of the National Institutes of Health, Public Health Service.