Table 7. *Torsion angles about* C(24)–C(23) *in vinbarbital and in analogous systems in other crystal structures**

Atoms in the several molecules being compared with vinbarbital are numbered according to the conventions adopted by the respective authors. The torsion angles are defined in the same way as shown in Fig. 5.

Compound	Atoms	Angle
Vinbarbital	C(24)–C(23)	58·6°
Geranylamine hydrochloride†	C(6)—C(5)	47
Harunganin‡	C(26)–C(16)	60
	C(31)–C(16)	51
Rubber§	C(4)—C(6)	48·7
	C(9)—C(1)	49·7
Oleic acid‖	C(8)—C(7)	48·6
	C(11)–C(12)	51·5

* This is not an exhaustive table
† Jeffrey (1945)
‡ Alden, *et al.* (1964)
§ Nyburg (1954)
‖ Abrahamsson & Ryderstedt-Nahringbauer (1962)

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NH_4LiSO_4: A Variant of the General Tridymite Structure

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The crystal structure of the pseudohexagonal form of NH_4LiSO_4 has been determined and refined to an R index of 5.0% with 364 counter-diffractometer measured reflections. The space group is $P2_1cn$ with $a=5.280$ (2), $b=9.140$ (7), $c=8.786$ (6) Å and $Z=4$. SO_4 and LiO_4 tetrahedra share corners to form a framework enclosing large cavities which contain the NH_4 groups. The tetrahedral framework differs from that of $KLiSO_4$ (a tridymite derivative structure) by inversion of two tetrahedra in each of the six-membered rings of tetrahedra. The inversion of these tetrahedra leads to the formation of chains of four-membered rings of tetrahedra and modification of the shape of the large cavity, relative to the $KLiSO_4$ structure.

Introduction

Ammonium lithium sulfate, NH_4LiSO_4, is reported (Wyrouboff, 1890), to be polymorphous. The form crystallizing from an aqueous solution above room temperature is orthohombic, pseudohexagonal, and based on its morphological cell and pseudosymmetry is evidently related to the hexagonal compounds $KLiSO_4$ and $RbLiSO_4$. The crystal structure of $KLiSO_4$ (Bradley, 1925) shows that it is a derivative structure of tridymite, SiO_2, with LiO_4 and SO_4 tetrahedra arranged in a tridymite-like framework, and K atoms occupying the large cavities of the framework (this latter site is, of course, unoccupied in tridymite itself).

The present investigation was undertaken to determine the relationship of the pseudohexagonal form of NH_4LiSO_4 to the $KLiSO_4$ structure, *i.e.* its relationship to the general tridymite structure – in order to further understanding of this important structure type.

Crystal data and data collection

NH_4LiSO_4 was crystallized at about 25°C from an aqueous solution prepared from equimolar amounts of reagent grade $(NH_4)_2SO_4$ and $Li_2SO_4.H_2O$ dissolved in distilled water. The pseudohexagonal plates that form are almost invariably sector twinned, the sectors being related by a 120° rotation about the twin axis, which is coincident with the morphologic pseudohexagonal axis. Small crystal fragments were broken from individual sectors in order to obtain untwinned material.

The diffraction symmetry determined from precession photographs is *mmmP-cn*, which allows both space groups *Pmcn* and *P*2$_1$*cn*. The cell dimensions, measured on precession photographs on which a pattern from an NaF crystal was superimposed, are $a = 5{\cdot}280(2)$, $b = 9{\cdot}140(7)$ and $c = 8{\cdot}786(6)$ Å, using the value of 4·6342 Å for the NaF cell edge (Swanson & Tatge, 1953). The estimated standard deviations, referring to the last digit, are given in parentheses. The cell-edge ratios then are 1:1·7311:1·6640, compared with values of 1:1·7303:1·6679 previously determined from the morphology (Wyrouboff, 1890). As expected, the cell dimensions are closely related to those of hexagonal $KLiSO_4$ with $a_0 \simeq a_h$, $b_0 \simeq \sqrt{3}a_h$ and $c_0 \simeq c_h$. Assuming four formula units per unit cell, in analogy to the $KLiSO_4$ structure, the calculated density is 1·896 $g.cm^{-3}$ in agreement with the value of 1·889 measured by Wyroboff (1890).

Although the cells are closely related, the diffraction symbol shows that NH_4LiSO_4 cannot be a true derivative structure of tridymite. This follows from the safe assumption that the SO_4 and LiO_4 tetrahedra, if linked in the structure, must alternate.* Such alternation of tetrahedra in a tridymite-like arrangement leads to all SO_4 tetrahedra pointing one way along the *c* axis and all LiO_4 tetrahedra pointing in the opposite direction (as found in $KLiSO_4$). However, the presence of an *n* glide plane normal to **c** in NH_4LiSO_4 is obviously not consistent with this arrangement.

A crystal fragment of approximately 0·15 × 0·16 × 0·21 mm was selected for intensity measurements. These were made on an equi-inclination type, single-crystal diffractometer with Zr-filtered Mo $K\alpha$ radiation. The measurements were corrected for background and Lp factors but not for absorption, which was considered negligible ($\mu R = 0{\cdot}06$). A total of 364 independent reflections were measured, consisting of all available data up to $(\sin\theta)/\lambda \sim 0{\cdot}6$ Å^{-1}. Three of these reflections were considered to be not significantly above background and assigned zero intensity.

Along with the intensity measurements a check was made on the possible extent of twinning in the particular grain chosen. The very strong 121 reflection was

Table 1. *Observed and calculated structure factors*

Values of 100 F_o and 100 F_c are listed.

K	L	FOBS	FCAL
		H = 0	
2	0	3360	3950
4	0	747	327
6	0	4926	5068
8	0	2507	2314
10	0	1009	1011
12	0	741	711
2	1	5628	5814
3	1	1140	820
4	1	2027	2031
5	1	3522	3311
6	1	1293	1377
7	1	358	124
8	1	3050	3072
9	1	564	445
10	1	1434	1432
1	2	1253	1172
2	2	5539	5265
3	2	2946	2856
4	2	707	661
5	2	516	436
6	2	3003	2945
7	2	945	824
8	2	1756	1679
9	2	934	962
10	2	99	119
1	3	2139	2151
2	3	2013	1393
3	3	1008	657
4	3	724	795
5	3	1818	1833
6	3	810	860
7	3	2378	2404
8	3	2095	2145
9	3	337	241
1	4	281	171
2	4	1292	1332
3	4	1794	1894
4	4	1538	1418
5	4	821	789
6	4	2005	1853
7	4	1079	977
8	4	1173	1128
9	4	1543	1537
1	5	3140	3039
2	5	2350	2246
3	5	500	606
4	5	835	736
5	5	4103	4181
6	5	184	098
8	5	1049	1109
		H = 0	
1	6	1510	1557
2	6	1361	1245
3	6	3601	3572
4	6	896	957
5	6	918	867
6	6	1158	563
7	6	1422	1401
8	6	158	020
1	7	1961	1944
2	7	1385	1383
3	7	468	502
4	7	1063	1124
5	7	1777	1824
6	7	240	101
7	7	1807	1533
1	8	330	225
2	8	833	796
3	8	1213	1205
4	8	1588	1857
5	8	164	434
6	8	1242	1331
1	9	049	057
2	9	938	945
3	9	314	342
4	9	1020	1095
		H = 1	
1	0	3671	4305
3	0	6536	7048
5	0	2613	2553
7	0	3019	2974
9	0	2614	2702
11	0	967	1020
1	1	5588	5671
2	1	4637	4253
3	1	452	470
4	1	1003	946
5	1	1392	1659
6	1	335	474
7	1	2760	2801
8	1	1399	1496
9	1	700	769
10	1	291	301
0	2	2975	2885
1	2	4925	4501
2	2	1812	1735
3	2	3909	3625
4	2	1421	1373
5	2	2624	2521
		H = 1	
6	2	1523	1466
7	2	2025	2158
8	2	451	535
9	2	2407	2454
1	3	2307	2237
2	3	1002	1053
3	3	226	251
4	3	3342	3329
5	3	1150	1058
6	3	1025	1092
7	3	1315	1351
8	3	1143	1085
9	3	521	510
0	4	870	893
1	4	637	549
2	4	1510	1549
3	4	2858	2685
4	4	875	852
5	4	1158	1471
6	4	1315	1565
7	4	1450	1515
8	4	542	940
9	4	618	619
1	5	2369	2254
2	5	3507	3619
3	5	968	130
4	5	2703	2545
5	5	856	810
6	5	00	182
7	5	749	745
8	5	2275	2295
0	6	3604	3577
1	6	564	531
2	6	2101	2016
3	6	2622	2637
4	6	1873	1909
5	6	960	1023
6	6	2452	2451
7	6	761	791
1	7	1214	1259
2	7	1661	1596
3	7	311	271
4	7	2344	2338
5	7	1318	1312
6	7	711	762
7	7	760	649
0	8	952	893
1	8	1723	1717
2	8	873	823
3	8	1935	2068
		H = 1	
4	8	593	680
5	8	1215	1225
1	9	916	907
2	9	403	403
3	9	140	067
		H = 2	
0	0	7348	7707
2	0	2030	1665
4	0	3034	3019
6	0	3617	3715
8	0	867	897
10	0	1552	1359
12	0	1525	1654
1	1	2573	2585
2	1	2555	2529
3	1	762	712
4	1	2275	2172
5	1	2572	2423
6	1	99	115
7	1	185	222
8	1	2145	2218
9	1	313	375
0	2	3643	3653
1	2	1372	1232
2	2	453	335
3	2	2423	2256
4	2	2440	2471
5	2	724	721
6	2	2076	2037
7	2	613	564
8	2	488	375
9	2	813	924
1	3	2543	2511
2	3	418	471
3	3	383	327
4	3	1383	1310
5	3	1278	1206
6	3	067	034
7	3	2151	2163
8	3	1449	1545
9	3	448	388
0	4	2831	2712
1	4	703	627
2	4	1878	1328
3	4	1871	1898
4	4	1180	1150
5	4	1110	1144
6	4	1194	1115
		H = 2	
7	4	752	640
8	4	160	174
1	5	3363	3335
2	5	1015	1032
3	5	834	906
4	5	836	826
5	5	3125	3124
6	5	321	345
7	5	1415	1433
8	5	711	736
9	5	3105	3103
1	6	1760	1720
2	6	966	1041
3	6	3271	3301
4	6	533	552
5	6	1245	1215
6	6	1053	955
7	6	1025	952
1	7	2373	2355
2	7	1707	[illegible]
3	7	255	152
4	7	1205	1411
5	7	1118	1102
6	7	257	167
0	8	2345	2442
1	8	505	512
2	8	1032	1055
3	8	1218	1311
4	8	1161	1190
1	9	543	491
2	9	1142	1131
		H = 3	
1	0	2555	2550
3	0	6154	6591
5	0	2621	2524
7	0	1052	[illegible]
9	0	1517	1512
11	0	858	964
1	1	2349	2175
2	1	2570	2517
3	1	625	735
4	1	761	661
5	1	2690	2673
6	1	476	457
7	1	2011	2031
8	1	1153	1206
0	2	2143	2102
1	2	2741	2678
		H = 3	
2	2	1016	905
3	2	2527	2432
4	2	903	801
5	2	2598	2626
6	2	1203	1165
7	2	465	452
8	2	432	434
1	3	1338	1314
2	3	1620	1557
3	3	434	434
4	3	2485	2454
5	3	1603	1675
6	3	634	676
7	3	1438	1456
8	3	1151	1166
0	4	1745	1616
1	4	582	569
2	4	1101	[illegible]
3	4	[illegible]	2065
4	4	546	631
5	4	1293	1313
6	4	1570	1588
7	4	218	231
1	5	1008	832
2	5	3145	3163
3	5	613	610
4	5	2100	[illegible]
5	5	[illegible]	1141
6	5	552	525
7	5	659	635
8	5	3244	3215
1	6	607	659
2	6	1425	1423
3	6	734	746
4	6	1204	1315
5	6	751	773
6	6	1312	1367
1	7	1634	1673
2	7	1672	1665
3	7	267	272
4	7	1927	1955
5	7	665	674
0	8	1232	1175
1	8	1346	1332
2	8	641	644
3	8	1165	1135
		H = 4	
0	0	4730	4763
2	0	2698	2727
4	0	2196	1744
6	0	2888	2846
8	0	1207	1281
10	0	936	922
1	1	1339	1238
2	1	2814	2748
3	1	313	205
4	1	3412	3418
5	1	1577	1487
6	1	929	879
7	1	303	342
0	2	1397	1285
1	2	1023	932
2	2	2660	2745
3	2	1369	1314
4	2	1466	1522
5	2	591	561
6	2	1723	1789
7	2	570	524
1	3	1577	1608
2	3	1549	1551
3	3	625	617
4	3	2316	2379
5	3	1137	1059
6	3	553	615
0	4	1875	1925
1	4	920	852
2	4	1227	1275
3	4	1429	1439
4	4	551	427
5	4	941	832
6	4	991	978
1	5	2031	2047
2	5	1221	1276
3	5	231	222
4	5	1423	1413
5	5	2273	2326
6	5	1293	1226
1	6	1504	1154
2	6	725	651
3	6	2165	2233
4	6	269	206
1	7	1421	1412
2	7	675	669
		H = 5	
1	0	531	410
3	0	3362	3381
5	0	552	371
7	0	1241	1305
9	0	1570	1632
1	1	2084	2173
2	1	1390	1326
3	1	805	910
4	1	450	407
5	1	1645	1653
0	2	1288	1294
1	2	704	680
2	2	465	393
3	2	1507	1480
4	2	613	559
5	2	519	435
1	3	1392	1426
2	3	1362	1303
3	3	738	763
4	3	1569	1695
0	4	1425	1333
1	4	476	398
2	4	504	491
3	4	1245	1207
1	5	1004	1084
		H = 6	
0	0	2395	2391
2	0	1178	1127
4	0	1107	1066
6	0	1528	1537
		H = 7	
1	0	660	516
3	0	2038	2116

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* Non-alternation would give polysulphate groups which would have hydrolyzed in the aqueous solution from which the compound crystallized.

measured at the positions where this reflection would occur if the grain were twinned as described above; no measurable intensity was recorded. It can be estimated then that no more than 0·1% of the volume of the grain could be present in twinned orientation.

Structure determination

A three-dimensional Patterson function was calculated and the four sulfur atoms present in the unit cell were identified as belonging to a single position. This position could either be the general one in $P2_1cn$ or the position on the mirror plane in $Pmcn$. With the signs for F calculated from the y and z coordinates of the sulfur atoms, an electron-density projection onto the centric (100) plane was computed. The oxygen atoms of the sulphate group were found; from their locations it could be determined that the SO_4 tetrahedron is not lying on a mirror plane, thereby restricting the space group to $P2_1cn$. From assumed bond lengths the x coordinates of the oxygen atoms were estimated and used in first calculating three-dimensional structure factors and subsequently a three-dimensional electron-density map. This map revealed the locations of the N and Li atoms. At this point full-matrix, least-squares refinement was instituted.

In the calculations scattering curves for neutral atoms were taken from the tabulation by Ibers (1962). Equal weights were used throughout, the quantity minimized being $\Sigma(|F_o|-|F_c|)^2$. On the basis of the strong anisotropy indicated in a late stage difference-Fourier synthesis, anisotropic thermal parameters of the oxygen atoms were included in the refinement. The final R index, for all reflections, is 5·0%. Observed and calculated structure factors are listed in Table 1. The positional and thermal parameters are listed in Table 2. The dimensions and orientations of the thermal vibration ellipsoids, derived from the thermal parameters, are also listed.

The hydrogen atoms were not located. A difference map computed after the refinement showed maximum anomalies of $\sim 0·3$ e.Å^{-3}. As these irregular maxima were located near the nitrogen atom, they may represent hydrogen atoms; however attempts at including trial hydrogen positions in the model improved neither the overall agreement nor the appearance of the difference map and refinement tended to shift the atoms to positions which gave highly improbable N–H distances. It must be concluded that either the hydrogen atoms are spatially disordered or, much more likely, the present data are insufficiently accurate to reveal their locations.

Description of the structure

In the structure of NH_4LiSO_4 (Fig. 1), the sulfur and lithium atoms are, as expected, tetrahedrally coordi-

Table 2. NH_4LiSO_4 *positional and thermal parameters*

Estimated standard deviations in parentheses.

	x	y	z	B
NH_4	0·4912 (25)	0·2137 (7)	0·4999 (7)	1·8 (1) Å^2
Li	0·0084 (73)	0·4117 (14)	0·3234 (15)	1·5 (2)
S	0†	0·0836 (2)	0·2030 (2)	0·90 (4)
O(1)	0·0003 (33)	0·0961 (10)	0·0384 (7)	*
O(2)	0·3323 (15)	0·4631 (7)	0·2496 (9)	*
O(3)	0·2585 (15)	0·0537 (7)	0·2565 (9)	*
O(4)	0·9059 (16)	0·2191 (7)	0·2705 (11)	*

* Anisotropic temperature factors of the form $(b_{11}h^2+\ldots 2b_{12}hk+\ldots)$.

† Fixed, to define x axis origin.

	b_{11}	b_{22}	b_{33}	$2b_{12}$	$2b_{13}$	$2b_{23}$
O(1)	0·028 (3)	0·030 (2)	0·003 (1)	−0·004 (4)	0·001 (3)	0·003 (1)
O(2)	0·016 (3)	0·006 (1)	0·011 (1)	−0·005 (1)	0·006 (2)	−0·004 (1)
O(3)	0·009 (2)	0·007 (1)	0·009 (1)	0·002 (1)	−0·004 (1)	−0·004 (1)
O(4)	0·019 (3)	0·004 (1)	0·021 (2)	0·001 (1)	0·002 (2)	−0·004 (1)

	Ellipsoid axis	R.m.s. amplitude	φa‡	φb	φc
O(1)	1	0·20 (1) Å	9 (12)°	86 (6)°	82 (13)°
	2	0·36 (1)	95 (7)	8 (4)	84 (2)
	3	0·09 (2)	97 (13)	97 (2)	10 (9)
O(2)	1	0·11 (2)	44 (21)	46 (20)	88 (20)
	2	0·13 (2)	122 (24)	59 (24)	48 (4)
	3	0·25 (1)	64 (4)	120 (4)	42 (4)
O(3)	1	0·10 (2)	23 (15)	87 (19)	67 (13)
	2	0·13 (2)	105 (21)	35 (6)	60 (11)
	3	0·23 (1)	107 (5)	125 (5)	40 (5)
O(4)	1	0·17 (1)	16 (10)	74 (10)	90 (4)
	2	0·10 (2)	106 (10)	21 (8)	77 (3)
	3	0·29 (1)	86 (4)	103 (3)	13 (3)

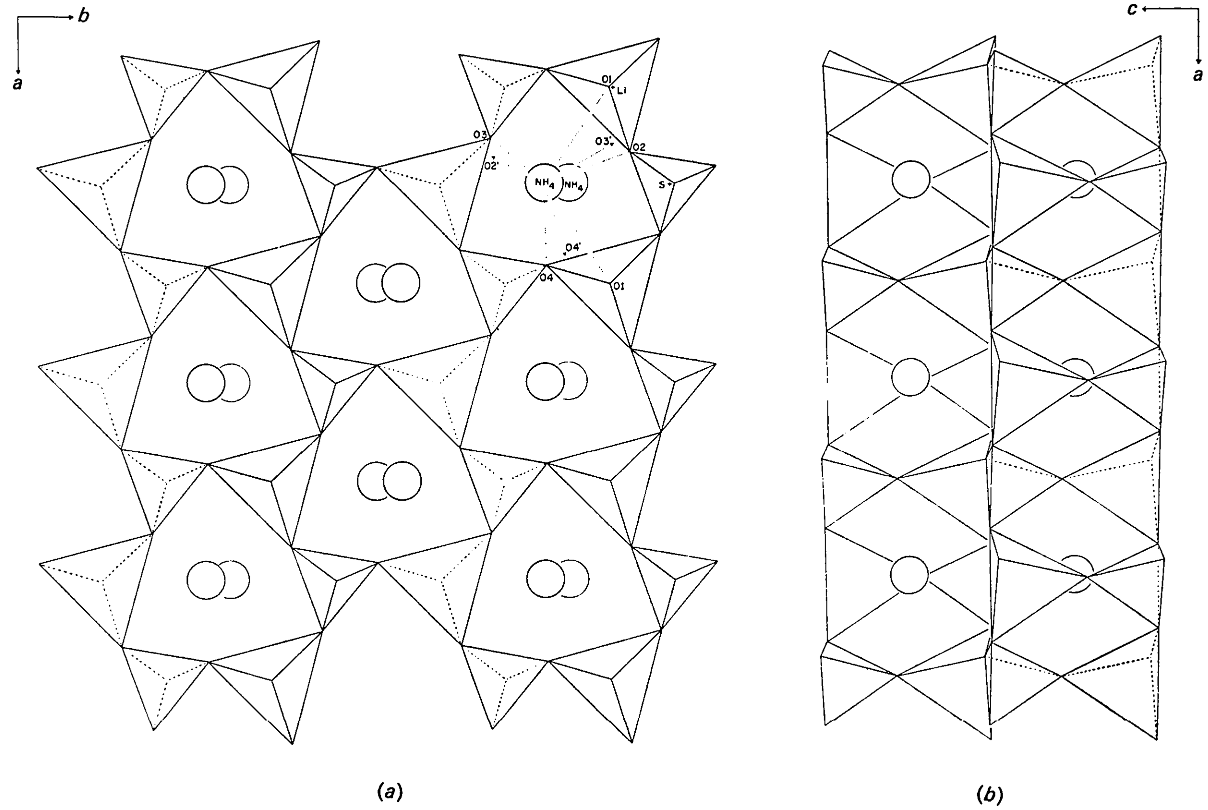
‡ The φ's are the angles between the ellipsoid axes and the cell axes.

nated, with each SO_4 tetrahedron sharing all of its corners with LiO_4 tetrahedra and *vice versa.* As seen in the Figure, the NH_4LiSO_4 tetrahedral framework and the tridymite framework are topologically the same in the *c*-axis projection. The differences between the structures stem from the fact that, in each six-membered ring of tetrahedra in NH_4LiSO_4, three *adjacent* tetrahedra point 'up' the *c* axis while the other three, forming the other half of the ring, point 'down'. In contrast, in the tridymite-like arrangement, adjacent tetrahedra point in opposite directions along the *c* axis. Thus the sequence of 'up' and 'down' tetrahedra in tridymite derivative structures is *UDUDUD* whereas in NH_4LiSO_4 the sequence is *UUUDDD*.

The successive layers of tetrahedral rings are almost exactly eclipsed as viewed along the *c* axis. The individual layers are joined parallel to the *c* axis by connecting tetrahedra in one layer that point down with those in the next lower layer that point up, and so forth. One consequence of neighboring tetrahedra pointing the same way is the formation of four-membered rings of tetrahedra. As seen in the Figure, these rings form a dense double-chain of tetrahedra running along the *a* axis. In a tridymite-like arrangement, only six-membered rings are formed in this orientation.

The NH_4 groups lie approximately at the centers of the large cavities in the tetrahedral framework. The group is eightfold coordinated with six oxygen atoms forming the corners of a truncated trigonal prism and two equatorial oxygen atoms lying outside two of the prism faces. Each of the oxygen atoms in the structure is coordinated to one Li, one S and two NH_4 groups. Interatomic distances and angles are listed in Table 3.

If the NH_4LiSO_4 structure were transformed to a tridymite-like arrangement by inversion of some of the tetrahedra, the NH_4–O bond lengths would remain essentially the same but the coordination number of the NH_4 group would increase to nine and O(1) would become five-coordinated. This, however, assumes that the S–O(1)–Li bond would remain nearly linear. In some of the actual tridymite derivative structures, such as kalsilite $KAlSiO_4$ (Perrotta & Smith, 1965), which is isostructural with $KLiSO_4$ but more accurately known, and nepheline $Na_3KAl_4Si_4O_{16}$ (Hahn & Buerger, 1955), the analogous *T*–O–*T*′ bond is bent away from a linear arrangement, reducing the respective coordination



(*a*) (*b*)

Fig. 1. NH_4LiSO_4 polyhedral linkage. (*a*) View along the *c* axis. Only one tetrahedral layer is shown. In successive layers, which are almost exactly eclipsed in this view, a LiO_4 tetrahedron pointing up is replaced by a SO_4 tetrahedron pointing down, *etc.* Fractional coordinates (*z*) of labeled atoms are NH_4 (heavy circle) 0·50 and (light circle) 0·00, O(1) 0·51, O(2) 0·25, O(2′) 0·75, O(3) 0·26, O(3′) 0·76, O(4) 0·27, O(4′) 0·77, Li 0·32, S 0·30. (*b*) *b*-axis view of 'double chain' of tetrahedra.

Table 3. *Bond lengths and angles*

Bonds	Uncorrected length	E.s.d.	Corrected* length
S–O(1)	1·450 Å	0·007 Å	1·496 Å
–O(2)	1·474	0·008	1·493
–O(3)	1·469	0·008	1·490
–O(4)	1·460	0·007	1·489
Li–O(1)	1·891	0·105	
–O(2)	1·889	0·036	
–O(3)	1·979	0·028	
–O(4)	1·899	0·018	
NH_4–O(1)	3·139	0·019	
–O(1′)	3·219	0·019	
–O(2)	3·277	0·010	
–O(2′)	2·851	0·011	
–O(3)	2·867	0·011	
–O(3′)	3·333	0·011	
–O(4)	2·976	0·014	
–O(4′)	3·290	0·013	

* Assuming oxygen atoms 'riding' on sulfur atoms.

Bonds	Angle	E.s.d.
O(1)–S—O(2)	110·0°	0·7°
O(1)–S—O(3)	109·4	0·8
O(1)–S—O(4)	109·8	0·6
O(2)–S—O(3)	109·2	0·5
O(2)–S—O(4)	108·3	0·5
O(3)–S—O(4)	110·1	0·5
O(1)–Li–O(2)	111·9	2·0
O(1)–Li–O(3)	111·3	2·0
O(1)–Li–O(4)	101·7	1·3
O(2)–Li–O(3)	108·6	1·9
O(2)–Li–O(4)	113·9	2·0
O(3)–Li–O(4)	109·4	1·3
S—O(1)–Li	173·2	1·7
S—O(2)–Li	129·3	0·7
S—O(3)–Li	128·9	0·7
S—O(4)–Li	142·0	1·3

numbers to eight and four. The bending of the *T*–O–*T′* bond angle could be interpreted as an attempt by this oxygen atom to retain fourfold or smaller coordination. In NH_4LiSO_4 and in orthorhombic high tridymite (Dollase, 1967) such bending is unnecessary to retain four-fold-or-less coordination, and the respective *T*–O–*T′* angles are 173·2 ± 1·7° and 178.7 ± 0·9°.

It is not evident why NH_4LiSO_4 adopts this structure rather than forming a tridymite-derivative structure. Perhaps this is only related to a favorable disposition of N–H. . . O bonds. There does not, however, seem to be any reason why this structure could not form with spherically symmetric atoms such as Rb in the cavities. Therefore the possibility of NH_4LiSO_4-like tetrahedral arrangements should be considered for some of the numerous compounds that appear to be tridymite-derivative structures on the basis of their cell dimensions and pseudosymmetry (see, *e.g.* Deer, Howie & Zussman, 1963). Even more generally, such a unit cell and (pseudo) symmetry relationship should be considered as only suggesting (pseudo) hexagonal layers of six-membered tetrahedral rings with successive layers joined by those tetrahedra pointing up being connected to tetrahedra in the next layer that point down. These structural aspects would give rise to a tridymite-like cell. The disposition of the tetrahedra in any one of these six-membered rings is not fixed by these relationships. In such six-membered rings there are only eight topologically different arrangements of tetrahedra that point either up or down. Any one of these should be considered possible in unknown structures. Besides the two demonstrated in this paper, the only other arrangement with three tetrahedra pointing in the same direction, namely *UUDDUD*, has, in fact, been proposed (Kunze, 1954) to exist in orthorhombic $KAlSiO_4$, although the structure has not been determined. Another of the eight possibilities, the arrangement with all tetrahedra in a ring pointing in the same direction (*UUUUUU*), exists in hexagonal $CaAl_2Si_2O_8$ and related structures (Takéuchi & Donnay, 1959) .

Thermal motion and bond-length corrections

The observed orientations of the thermal ellipsoids (long axes roughly normal to the S–O bonds and short axes roughly parallel to the S–O bonds) are consistent with a rigid-body librational motion of the sulfate tetrahedra. Values of the S–O bond lengths corrected for a model of oxygen atoms 'riding on' sulfur atoms are included in the Table. As the magnitude of the vibration is large, the corrections are significantly larger than the formal standard deviations in the bond lengths The vibrational ellipsoids do not indicate that such a correlated-motion model is applicable in the case of the weaker-bonded LiO_4 and NH_4O_8 polyhedra.

The vibrational ellipsoid of the O(1) atom deserves a further comment. The smallest vibration amplitude is approximately in the *c*-axis direction, along the S–O(1) bond. Vibration in the *ab* plane, however, is also very anisotropic and is apparently influenced by the near non-bonded neighbors in the four-member tetrahedral rings such that vibration of O(1) normal to the approximate 'plane' of the chain-forming rings is almost twice that parallel to the chain direction (see Fig. 1).

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