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X-Ray Structure Analysis of Sodium Hydrogen Sulphate Monohydrate

BY G. E. PRINGLE AND T. A. BROADBENT

School of Chemistry, University of Leeds, England

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The crystal structure of sodium hydrogen sulphate monohydrate at room temperature has been determined by three-dimensional methods. There are four formula units in a monoclinic unit cell which has $a = 8{\cdot}217 \pm 0{\cdot}005$, $b = 7{\cdot}788 \pm 0{\cdot}005$, $c = 7{\cdot}814 \pm 0{\cdot}005$ Å; $\beta = 119° \; 56' \pm 5'$ and space group *Aa*.

The structure has been refined by the method of least squares with allowance for anisotropic thermal vibration for all atoms but those of hydrogen. The final *R* value is 0·103.

In the distorted tetrahedron of the SO_4 group the S–O(H) distance is longer by 0·16 Å than the other S–O distances. S–O(H) = 1·61 Å and S–O = 1·45 Å after correction for rotational oscillation. The anions are linked by the acidic hydrogen atoms to form chains in the [101] mean direction. The water molecules link these chains transversely by hydrogen bonding to the remaining oxygen atoms, forming chains in the [011] direction.

Six oxygen atoms surround each Na^+ ion in an irregular octahedron. The lone pairs on water molecules point approximately to two Na^+ ions.

Introduction

The inorganic sulphates and hydrogen sulphates present a diversity of structures of which relatively few have been fully examined; isomorphism does not appear to reduce the problem to manageable size, especially as the numbers are swollen by a long list of hydrates.

The anhydrous and hydrated sodium hydrogen sulphates are two of the structures hitherto unknown; we have chosen the latter to investigate because the hydrogen bonding of the water molecule is of some interest and has not so far been successfully studied by proton resonance. Owing to the low acid strength of the HSO_4^- anion one hardly expects the oxonium ion to be present in a structurally significant degree; yet the water oxygen might have proved to be bonded loosely to the acidic hydrogen. In the event, this possibility is disproved since the water is hydrogen-bonded to only two other oxygen atoms; perhaps this too could have been foreseen by inspection of the formula $NaHSO_4 . H_2O$, since if each H is coordinated to two O, of which there are only five altogether, it seems likely that one of the latter is coordinated to two H, and the rest to one each only.

This conclusion may be compared with thermochemical data. Standard heat of hydration is perhaps less helpful here than heat of hydration by water vapour, *i.e.* 12·0 cal.mole^{-1}. (National Bureau of Standards Circular 500) approximately corresponding to the formation of two hydrogen bonds by each water molecule. We therefore suppose that the electrostatic lattice energy is not grossly affected by the hydration.

Experimental

Crystals were obtained from a solution of $NaHSO_4$ in 45% sulphuric acid, and being deliquescent were sealed into glass capillary tubes.

Cu $K\alpha$ radiation was used for all diffraction measurements. Unit-cell dimensions were obtained from Weissenberg photographs on which were superimposed powder patterns from copper and aluminum wires. The values obtained were: $a = 8{\cdot}217 \pm 0{\cdot}005$, $b = 7{\cdot}788 \pm 0{\cdot}005$, $c = 7{\cdot}814 \pm 0{\cdot}005$ Å; $\beta = 119° \; 56' \pm 5'$.

Permitted reflexions (*hkl* with $k+l$ even, *h*0*l* with *h* even) corresponded to space groups *Aa* or *A*2/*a*. With 4 molecules in the unit cell, the calculated density is 2·12 compared with 2·10 found by direct determination.

The crystals used in gathering intensity data were dipped into liquid nitrogen so that the thermal shock would improve their mosaic quality and reduce extinction effects. They were chosen to be as nearly spherical as possible with no dimension greater than 0·15 mm. The linear absorption coefficient $\mu = 60$ cm^{-1}.

Equi-inclination Weissenberg photographs were taken about the *a*, *b* and [110] axes (5,5 and 3 layers respectively). A multiple-film technique was used and the intensities were estimated visually.

The following calculations on the Leeds University Pegasus computer were made by means of programs written by Mr J. G. F. Smith:

(*a*) Application of Lorentz and polarization factors.

(*b*) Corrections to non-zero layers on which only the elongated spots were measured (Phillips, 1954).

(*c*) Correlation of layer lines by the least-squares method of Rollett & Sparks (1960).

Structure determination

Of the two possible space groups, *Aa* and *A*2/*a*, the former is chosen since in *A*2/*a* the atoms would have to be in special positions and it would be impossible to form a reasonable sulphate tetrahedron. *Aa* has fourfold general positions. It was also noticed that the structure is pseudo-tetragonal approximating to $I\bar{4}2d$, the 'unique axis' being the [201] monoclinic axis.

Patterson syntheses of projections along the *a* and *b* axes gave vector maps showing peaks identified as corresponding to S–S, S–Na, S–O, and Na–Na vectors. These projections also confirmed that the space group is *Aa*. The sulphur atoms were placed unequivocally and the orientation of the SO_4 tetrahedron was found. The sodium ion was placed except for an ambiguity of sign in the *x* coordinate. A model showed that in one of these two positions the Na^+ would be too near the anions. However, one cycle of refinement in the [*h*0*l*] zone, with scale and temperature factors given by Wilson's method, resolved the ambiguity, and the lower agreement index was at this stage $R=0{\cdot}20$. With the phases so obtained a Fourier '*F*' synthesis using the observed structure amplitudes was computed with a program written by Pilling, Lovell & Bujosa (Cruickshank *et al.*, 1961); the resulting electron density map failed to reveal the water molecule which later proved to be eclipsed in the *a* and *b* projections.

At this stage an attempt was made to refine the atomic positions in three dimensions. In three cycles the *R* index fell from 0·36 to 0·31. Two of the oxygen positions would not refine at first until the water molecule had been located on a three-dimensional set of electron-density maps. Thereafter the refinement proceeded smoothly. The structure is shown in Fig. 1.

Refinement

Refinement was carried out by the method of least squares with a program written by Cruickshank & Pilling (Cruickshank *et al.*, 1961). The function minimized was $R=\Sigma w(|F_o|-|F_c|)^2$ where the weighting factor *w* was $1/|F_o|$. The scattering factor for sulphur was that of Tomiie & Stam (1958), for Na^+ that of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955), and that for $O^{\frac{1}{2}-}$ was obtained from curves for O and O^- of Berghuis *et al.* (1955).

When the *R* index had reached 0·25 anisotropic temperature factors were introduced for all the atoms. After six cycles of refinement *R* fell to 0·14.

A test for extinction was made by using observed and calculated intensities. A correction was applied to five reflexions assuming the Darwin formulae for secondary extinction but applying these to the two planes of polarization separately, as advocated by Zachariasen (1963).

Calculation of O–O distances was used to identify the hydrogen bonds in the structure; all the oxygen atoms participate in at least one such bond and the water oxygen in two. Since S–O(3) was clearly the longest S–O bond, the attachment of the acidic hydrogen was thereby determined. In this way, hydrogen atoms were

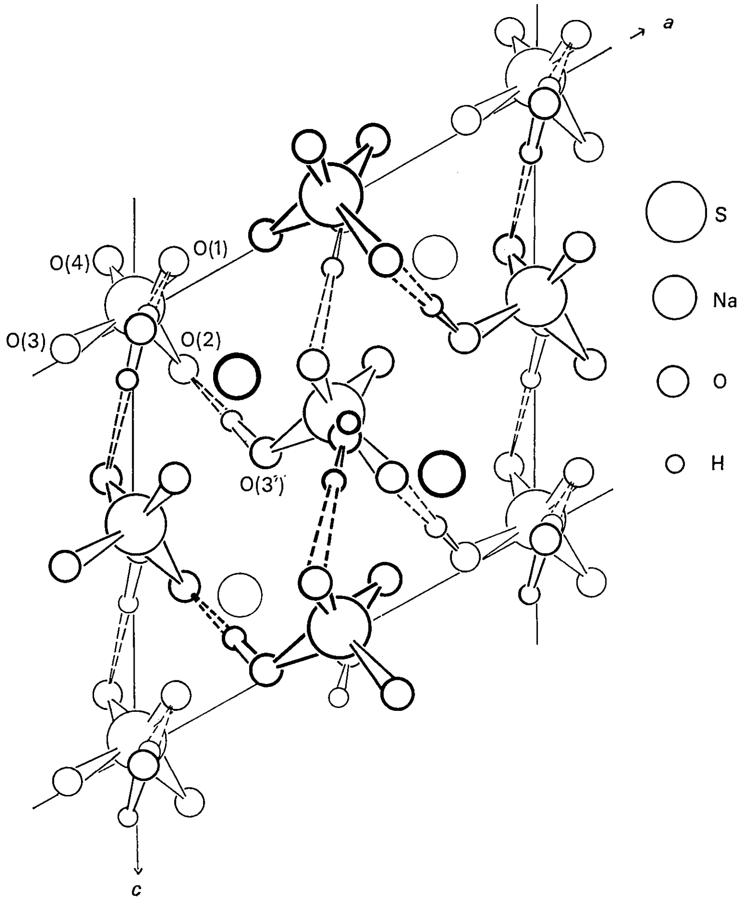

Fig. 1. Projection along *b* axis showing hydrogen bonds.

Table 1. *Observed and calculated structure factors*

0	0	-8	271	257	114	230
0	0	-6	285	275	261	88
0	0	-4	629	738	633	378
0	0	-2	415	612	512	335
0	1	-7	254	249	100	228
0	1	-5	325	294	249	156
0	1	-3	400	412	-237	337
0	1	-1	400	434	431	52
0	2	-8	136	142	-137	-36
0	2	-6	330	317	295	-115
0	2	-4	503	436	-350	-259
0	2	-2	255	203	-127	-159
0	2	0	346	313	-313	0
0	3	-7	249	231	-47	-226
0	3	-5	294	253	-179	-178
0	3	-3	513	535	-478	-240
0	3	-1	360	383	-286	255
0	4	-8	62	102	-45	-91
0	4	-6	325	288	-247	-148
0	4	-4	294	220	-192	-107
0	4	-2	519	530	-491	198
0	4	0	188	149	149	0
0	5	-5	332	299	-8	-299
0	5	-3	76	66	-62	22
0	5	-1	96	80	42	-68
0	6	-4	189	169	-107	-131
0	6	-2	115	108	-6	108
0	6	0	289	242	-242	0
0	7	-3	222	196	180	-78
0	7	-1	336	382	206	322
0	7	1	336	382	206	-322
0	8	-4	170	165	155	57
0	8	-2	279	308	229	206
0	8	0	274	297	297	0
1	1	-9	123	136	-129	-43
1	1	-7	316	291	-180	229
1	1	-5	237	213	-194	-87
1	1	-3	447	539	-247	479
1	1	-1	308	304	-20	303
1	1	1	795	898	179	880
1	1	3	460	447	447	0
1	1	5	453	502	384	324
1	1	7	224	227	201	-104
1	2	-8	191	124	-73	101
1	2	-6	370	399	-236	321
1	2	-4	439	428	-71	422
1	2	-2	579	688	107	679
1	2	0	919	907	56	905
1	2	2	444	443	-44	441
1	2	4	504	516	308	415
1	2	6	288	248	63	240
1	2	8	180	200	198	30
1	3	-7	205	186	-180	-46
1	3	-5	443	487	-394	285
1	3	-3	345	309	12	-309
1	3	-1	313	295	52	290
1	3	1	565	561	-254	-500
1	3	3	205	178	107	142
1	3	7	152	156	117	102
1	4	-6	141	124	102	70
1	4	-4	275	236	-193	-135
1	4	-2	315	291	291	20
1	4	0	476	456	-439	125
1	4	2	90	88	-27	-83
1	4	4	190	176	-124	125
1	5	-7	251	230	230	-10
1	5	-5	267	271	59	-265
1	5	-3	211	204	102	-176
1	5	-1	321	290	38	-288
1	5	1	171	129	-118	-53
1	5	3	328	283	74	-274
1	5	7	254	280	-148	-238
1	6	-6	102	147	89	-117
1	6	-4	322	324	303	-114
1	6	-2	325	279	98	-261
1	6	0	512	378	230	-300
1	6	2	380	364	-199	-304
1	6	4	270	214	77	-200
1	6	6	212	273	-243	-124
1	7	-5	128	112	101	47
1	7	-3	206	191	175	-75
1	7	-1	168	166	125	-109
1	7	1	224	244	-50	-239
1	7	3	159	136	-123	-58
1	7	5	155	187	-154	-106
1	8	0	193	200	-192	-56
1	8	4	62	73	-63	37
1	9	1	246	248	-16	248
1	9	3	214	275	32	273
1	10	0	138	175	133	114
2	0	-8	93	86	86	7
2	0	-6	491	513	510	58
2	0	-4	366	354	-339	-102
2	0	-2	1130	1139	1126	173
2	0	0	549	605	585	156
2	0	2	420	617	563	-252
2	0	4	322	294	280	-90
2	0	6	400	339	291	-174
2	1	-9	228	243	-68	233
2	1	-7	292	287	220	184
2	1	-5	276	248	-74	236
2	1	-3	149	128	-90	91
2	1	-1	577	594	549	226
2	1	1	370	340	-157	-301
2	1	3	245	180	18	-180
2	1	5	236	239	212	-111
2	1	7	186	233	1	-233
2	2	-8	206	156	130	87
2	2	-4	251	213	181	111
2	2	-2	178	149	137	59
2	2	0	509	589	588	-27
2	2	2	484	480	-480	-3
2	2	4	374	332	269	194
2	2	6	152	133	-29	130
2	3	-7	136	101	-29	-97
2	3	-5	393	355	-189	-301
2	3	-3	408	399	-357	179
2	3	-1	53	37	10	-36
2	3	1	324	277	-252	115
2	3	3	259	225	-217	56
2	3	5	269	254	-18	253
2	3	7	105	121	-107	58
2	4	-6	366	325	-81	-315
2	4	-4	635	707	-663	-247
2	4	-2	393	316	-294	117
2	4	0	533	548	-539	-96
2	4	2	226	240	-240	3
2	4	4	382	401	-377	137
2	4	6	193	96	-91	32
2	5	-7	279	287	6	-287
2	5	-5	234	246	-88	-230
2	5	-3	279	263	-71	-253
2	5	-1	123	108	-107	6
2	5	1	409	375	-157	-340
2	5	3	365	380	-215	314
2	5	5	98	116	-107	45
2	6	-6	36	39	-31	23
2	6	-4	173	132	117	60
2	6	-2	187	140	-87	110
2	6	0	205	233	79	-219
2	6	2	213	169	-168	-22
2	6	4	83	62	-22	58
2	7	-5	186	195	187	-54
2	7	-3	448	444	162	413
2	7	-1	286	300	300	-17
2	7	1	366	369	353	105
2	7	3	205	211	208	-38
2	7	5	177	216	213	-34
2	8	-6	117	122	104	64
2	8	-4	203	182	98	153
2	8	0	265	273	273	-15
2	8	2	259	279	279	-12
2	9	1	193	210	59	-201
3	1	-9	195	194	-171	92
3	1	-7	140	124	-89	-86
3	1	-5	182	178	-142	107
3	1	-3	476	489	32	-488
3	1	-1	384	402	-368	162
3	1	1	353	308	-145	-271
3	1	3	417	404	85	395
3	1	5	126	92	92	-2
3	2	-8	245	179	-157	87
3	2	-6	339	291	-185	224
3	2	-4	334	279	-131	246
3	2	-2	515	620	37	619
3	2	0	440	449	-270	358
3	2	2	429	385	167	347
3	2	4	367	347	-17	347
3	2	6	205	155	110	109
3	3	-9	215	169	-131	-107
3	3	-7	440	442	-394	200
3	3	-5	375	333	-322	-84
3	3	-3	557	592	-83	587
3	3	-1	162	135	-51	125
3	3	1	338	319	204	244
3	3	3	243	249	244	47
3	3	5	244	203	113	168
3	4	-6	180	153	-150	33
3	4	-4	276	278	258	103
3	4	-2	309	247	-139	204
3	4	0	90	81	-8	81
3	4	2	180	145	-59	132
3	4	4	132	131	57	118
3	4	6	93	109	-95	-53
3	5	-7	254	208	163	-129
3	5	-5	257	244	188	-156
3	5	-3	441	513	255	-445
3	5	-1	299	268	-97	-250
3	5	1	473	454	-94	-444
3	5	3	37	38	-35	-14
3	5	5	231	244	-118	-214
3	6	-6	286	263	231	-127
3	6	-4	313	303	87	-290
3	6	-2	429	408	290	-286
3	6	0	465	467	-157	-440
3	6	2	374	342	78	-333
3	6	4	308	321	-223	-232
3	7	-7	64	79	76	-21
3	7	-5	105	87	77	-40
3	7	-3	118	127	122	36
3	7	-1	185	147	72	-128
3	7	3	142	130	-40	-124
3	8	-6	137	159	-159	7
3	8	-4	212	106	57	89
3	8	-2	180	160	-157	-30
3	8	2	131	153	-100	116
3	9	-3	167	180	-99	150
3	9	-1	180	148	-50	140
3	9	1	278	279	-74	269
4	0	-10	156	174	-137	107
4	0	-8	472	422	342	247
4	0	-4	378	378	347	151
4	0	-2	511	440	222	380
4	0	0	526	489	424	243
4	0	2	263	233	170	160
4	0	4	477	561	544	137
4	0	6	141	160	93	-131
4	1	-9	197	206	46	201
4	1	-7	284	274	59	267
4	1	-5	237	205	-166	120
4	1	-3	395	385	200	329
4	1	-1	240	205	184	91
4	1	1	184	150	-48	-142
4	1	3	228	211	208	-38
4	1	5	136	144	113	-89
4	2	-6	231	138	138	1
4	2	-4	114	119	-115	-29
4	2	-2	619	735	732	70
4	2	0	395	346	-115	-326
4	2	2	240	230	157	-168
4	2	4	110	105	-99	35
4	2	6	59	66	-4	-66
4	3	-7	308	304	64	-297
4	3	-5	332	298	-232	-187
4	3	-3	261	227	-65	-218
4	3	-1	201	148	-136	-59
4	3	1	382	353	-874	-222
4	3	3	237	222	-148	166
4	3	5	144	121	-121	14
4	4	-6	451	438	-287	-330

Table 1 (*cont.*)

4	4	−4	329	294	−275	−104
4	4	−2	609	592	−589	−65
4	4	0	339	312	−312	−8
4	4	2	529	540	−499	207
4	4	4	156	186	−99	157
4	5	−7	164	168	−84	−146
4	5	−5	227	241	−75	−229
4	5	−3	259	260	−170	197
4	5	−1	258	226	−17	−225
4	5	1	273	260	−163	202
4	5	3	210	190	−161	101
4	6	−6	51	44	42	14
4	6	−4	232	225	−106	198
4	6	−2	184	147	145	25
4	6	0	100	144	38	−139
4	6	4	111	115	−37	−98
4	7	−7	153	193	190	−33
4	7	−5	258	234	146	182
4	7	−3	228	201	201	12
4	7	−1	298	280	272	64
4	7	1	248	250	233	−90
4	7	3	155	174	166	50
4	8	−4	227	178	118	133
4	8	−2	156	148	140	48
4	8	0	213	221	220	−16
4	8	2	127	139	132	44
4	9	−3	242	225	27	223
4	9	−1	153	162	135	−89
5	1	−9	232	216	−206	−65
5	1	−7	362	424	−368	210
5	1	−5	155	124	−116	−43
5	1	−3	428	445	−207	394
5	1	−1	267	212	−136	−162
5	1	1	360	346	−87	335
5	1	3	120	124	−43	116
5	1	5	220	254	86	239
5	2	−8	272	230	−197	119
5	2	−6	323	295	−275	105
5	2	−4	414	411	−89	401
5	2	−2	473	531	−348	401
5	2	0	403	370	−5	370
5	2	2	435	428	−37	427
5	2	4	295	248	51	242
5	3	−9	105	168	−151	74
5	3	−7	218	249	−181	−170
5	3	−5	224	170	−140	96
5	3	−3	136	131	−129	−22
5	3	−1	304	243	−95	224
5	3	1	247	216	214	29
5	3	3	253	265	142	224
5	4	−6	200	197	192	47
5	4	−4	119	105	98	38
5	4	−2	165	125	125	0
5	4	0	144	129	−51	−118
5	4	2	131	103	89	52
5	4	4	142	132	−118	−59
5	5	−5	273	304	253	−168
5	5	−3	166	172	160	−63
5	5	−1	437	443	47	−440
5	5	1	177	143	0	−143
5	5	3	239	221	−115	−189
5	6	−6	191	174	25	−172
5	6	−4	279	229	207	−98
5	6	−2	291	269	−119	−241
5	6	2	191	200	−125	−156
5	7	−7	102	133	98	−90
5	7	−5	105	101	99	−18
5	7	−3	113	111	24	−109
6	0	−10	192	263	105	242
6	0	−8	312	230	81	215
6	0	−6	407	425	367	214
6	0	−4	430	411	381	153
6	0	−2	566	663	653	116
6	0	0	235	184	136	−123
6	0	2	408	489	480	94
6	0	4	154	172	171	−19
6	1	−9	245	250	56	244
6	1	−7	146	145	−26	143
6	1	−5	221	191	2	191
6	1	−3	328	321	230	225
6	1	−1	122	74	74	−8
6	1	1	181	180	160	−83
6	1	3	180	166	165	15
6	2	−8	126	108	90	−59
6	2	−6	372	378	−326	−191
6	2	−4	195	167	69	152
6	2	−2	177	201	−187	74
6	2	0	130	94	93	−12
6	2	2	133	109	−82	73
6	3	−9	141	187	59	−177
6	3	−7	226	237	−126	−201
6	3	−5	291	295	−151	−254
6	3	−3	180	190	−188	−25
6	3	−1	260	338	−246	−231
6	3	1	287	287	−274	84
6	3	3	168	179	−166	67
6	4	−8	167	176	−48	−169
6	4	−6	135	143	14	−143
6	4	−4	168	276	−231	−150
6	4	−2	229	226	−67	−216
6	4	0	443	442	−425	−122
6	4	2	249	233	−223	68
6	5	−7	275	269	78	−257
6	5	−5	89	100	−91	41
6	5	−3	179	165	58	−154
6	5	1	112	95	−81	−49
6	6	−6	143	137	−133	37
6	6	−4	185	147	−69	130
6	7	−5	128	106	82	68
6	7	−3	184	172	86	149
7	1	−9	284	263	−251	78
7	1	−7	168	160	−158	−21
7	1	−5	398	409	−175	369
7	1	−3	88	97	17	95
7	1	−1	311	301	87	288
7	1	1	122	118	110	43
7	1	3	162	172	71	157
7	2	−8	226	212	−209	36
7	2	−6	233	210	−77	195
7	2	−4	350	338	−214	262
7	2	−3	251	199	−173	99
7	2	−2	304	276	−77	265
7	2	0	372	324	−45	321
7	2	2	293	288	22	287
7	3	−9	174	172	−149	−87
7	3	−7	147	157	−157	−3
7	3	−5	173	162	−87	−136
7	3	−3	272	283	−279	49
7	3	−1	172	134	−115	−69
7	3	1	280	292	−70	284
7	4	−4	80	83	51	66
7	4	−2	168	154	−111	−107
7	4	0	61	52	48	20
7	4	2	149	151	−151	−1
7	5	−7	175	163	132	−96
7	5	−5	137	166	150	71
7	5	−3	251	231	155	−171
7	5	−1	291	209	176	−113
7	5	1	198	210	74	−196
7	6	−6	218	271	271	−4
7	6	−4	194	171	71	−156
7	7	−5	157	153	119	−96
8	0	−8	214	169	77	150
8	0	−6	97	110	35	105
8	0	−4	449	476	408	246
8	0	−2	174	157	142	−67
8	0	0	335	327	326	−31
8	1	−9	149	148	8	148
8	1	−7	116	113	−52	100
8	1	−5	191	180	76	163
8	1	−3	141	141	63	126
8	1	−1	119	104	92	−49
8	1	1	120	140	128	57
8	2	−8	123	103	−49	−90
8	2	−6	118	79	78	10
8	2	−4	140	117	−107	47
8	2	−2	85	86	61	61
8	2	0	117	103	−52	88
8	3	−7	184	187	−35	−184
8	3	−5	96	94	−94	−12
8	3	−3	147	153	−48	−146
8	3	−1	182	156	−150	−43
8	3	1	121	134	−133	−5
8	4	−8	136	162	5	−162
8	4	−6	274	237	−191	−140
8	4	−4	112	119	−29	−115
8	4	−2	367	304	−215	−215
8	4	0	222	235	−206	−112
8	5	−7	160	144	−48	−136
8	5	−5	198	200	−52	−193
8	5	−3	110	108	−78	−74
8	6	−6	52	45	−28	35
8	6	−4	83	87	−87	1
9	1	−7	168	176	−176	8
9	1	−5	140	167	−150	−73
9	1	−3	188	216	−158	148
9	2	−8	108	105	−100	32
9	2	−6	181	180	−157	89
9	2	−4	212	186	−136	126
9	2	−2	197	192	−127	145
9	3	−7	58	70	−66	22
9	3	−5	214	194	−120	153
9	3	−3	42	59	−35	−47
9	3	−1	171	173	−48	166
9	4	−6	137	128	43	120
9	4	−4	77	70	−66	23
9	4	−2	104	112	88	69
9	5	−5	135	155	79	−134
9	5	−3	100	111	79	−78
10	0	−4	192	222	28	220
10	1	−7	107	111	0	111
10	1	−5	164	172	23	171
10	1	−3	64	72	57	44
10	2	−6	64	69	37	−58
10	2	−4	120	129	108	−71
10	3	−5	108	136	−6	−136

Table 2. *Fractional coordinates and standard deviations*

	x/a	y/b	z/c	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
S	0·005	0·129	−0·024	0·006	0·003	0·006
Na	−0·246	0·206	0·243	0·008	0·006	0·008
O(1)	0·956	0·258	−0·758	0·013	0·013	0·015
O(2)	0·119	0·697	0·181	0·014	0·012	0·013
O(3)	−0·170	0·213	−0·018	0·014	0·012	0·016
O(4)	−0·064	−0·011	−0·160	0·016	0·013	0·014
O(*W*)	0·009	0·091	0·525	0·015	0·014	0·012
H	−0·015	0·056	0·636			
H	0·040	0·017	0·497			
H	0·238	0·204	0·369			

given reasonable positions on the O–O vectors; the hydrogen coordinates would not refine and so were kept constant. The refinement was completed in a further three cycles when the value of R was 0·105; the largest shift in any parameter was 0·25 of the standard deviation. Table 1 shows the final observed and calculated structure factors, Table 2 the atomic coordinates and their standard deviations and Table 3 shows the final values for the tensor components describing the anisotropic vibration of the atoms. The tensor components U_{ij} are those occurring in the temperature factor

Table 3. *Thermal parameters* ($Å^2 \times 10^{-3}$)

	U_{11}	σ	U_{22}	σ	U_{33}	σ	U_{12}	σ	U_{23}	σ	U_{13}	
S	6	1	6	1	3	1	3	2	2	2	−3	2
Na	20	3	10	3	13	3	−5	5	9	5	14	5
O(1)	13	5	14	6	32	6	−13	10	−12	10	26	10
O(2)	22	6	19	6	1	4	−17	10	0	8	−7	8
O(3)	9	5	19	7	22	6	6	9	9		13	9
O(4)	38	8	14	5	10	5	−17	11	−12	9	18	9
O(*W*)	27	6	27	6	1	5	−21	10	−5	8	7	10

$$\exp\{-2\pi^2(h^2a^{*2}U_{11}+2hka^*b^*U_{12}\ \ldots)\}$$

so that for instance U_{11} is the mean square amplitude of vibration of the atom parallel to the a^* axis.

An analysis of the vibrational motion was carried out with a program written by Bujosa & Cruickshank (Cruickshank *et al.*, 1961). The results showed that the assumption that the SO_4 group moved as a rigid body was justified within experimental error, the index of difference between calculated and observed radial vibration amplitudes for these atoms being 0·003 Å (s.d.). Table 4 shows the translational and rotational amplitudes of the SO_4 motion. Corrections for the systematic errors in bond lengths caused by rotational oscillation were also calculated by this programme, using Cruickshank's (1961) formulae: the most significant change in any coordinate was 0·9 times the standard deviation. The corrected coordinates are given in Table 5.

Table 4. *Principal values and axes of the translational and rotational tensors w.r.t. standard orthogonal axes a, b, c**

Mean-square Amplitude of translation	Direction cosines of axes		
0·000 ± 0·002 $Å^2$	0·354	0·372	0·858
0·013 ± 0·002	−0·921	0·297	0·251
0·010 ± 0·002	0·161	0·879	−0·448

Root-mean-square angular oscillation	Direction cosines of axes		
1·9°	0·416	0·336	0·845
7·2	0·156	−0·942	0·298
4·8	0·896	0·008	−0·444

Table 5. *Corrected coordinates for* SO_4 (Å)

S	0·042	1·005	−0·187
O(1)	0·797	2·011	−0·589
O(2)	0·983	0·544	1·428
O(3)	−1·409	1·660	−0·142
O(4)	−0·535	−0·090	−1·267

Interatomic distances and angles

From the corrected coordinates the bond lengths and angles and all interatomic distances of less than 3·5 Å were calculated with a program written by Truter (Cruickshank *et al.*, 1961). A program written by Mr J. G. F. Smith was used to compute standard deviations in all distances and angles. Selected values are shown in Table 6.

The hydrogen bond involving the acidic hydrogen O(2)——O(3′) is 2·70 Å long whilst of those involving the water O(4)—O is 2·91 Å, and O—O(1) is 2·90 Å.

In the HSO_4 group there is no doubt that the hydrogen is attached to O(3) as S–O(3) = 1·613 Å compared with S–O(1) = 1·432 Å, S–O(2) = 1·478 Å, S–O(4) = 1·440 Å. The attachment of this hydrogen to O(3) is also supported by the O(3)–S–O(1,2,4) angles which are all less than tetrahedral. In considering the probable positions of the water hydrogen atoms the two distances quoted above were chosen as bonding distances, 0·2 Å less than any other water–oxygen distance. $Na^+ \cdots O$ distances range from 2·35 to 2·46 Å and are similar to other determined values (Sass & Scheuerman, 1962; Carpenter, 1952; Taylor & Beevers, 1952).

The lone pairs of each water molecule point approximately to two Na^+ ions, whereas those of the anion oxygen atoms form only one such link each. The coordination shell of the Na^+ ion is a distorted octahedron of oxygen atoms.

Discussion

The gross structure in terms of cations and anions (Fig. 2) shows 4:4 coordination with Na^+ near the centre of an approximately rectangular (4·23 Å × 5·52 Å) arrangement of sulphur atoms. Each anion is surrounded by four sodium ions at the corners of an irregular

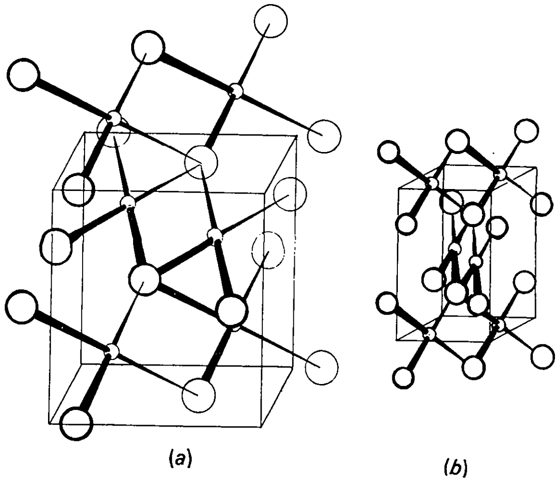

Fig. 2. (*a*) Gross structure of Na (small circles) and S (large circles) positions with *a* axis vertical, for comparison with (*b*) tenorite, CuO (monoclinic, space group *C*2/*c*) approximately to the same scale.

Table 6. *Selected bond lengths and angles*

S–O(1)	1·432 ± 0·013 Å	O(1)–S–O(2)	113° 14′ ± 1°
S–O(2)	1·478 ± 0·012	O(2)–S–O(4)	111 51 ± 1
S–O(3)	1·613 ± 0·013	O(1)–S–O(4)	113 06 ± 1
S–O(4)	1·440 ± 0·013	O(1)–S–O(3)	108 56 ± 1
O(3)–H · · · O(2)	2·70 ± 0·02	O(2)–S–O(3)	101 14 ± 1
O(1) · · · H–O(*W*)	2·90 ± 0·02	O(3)–S–O(4)	107 39 ± 1
O(4) · · · H–O(*W*)	2·91 ± 0·02		
Na^+–O(3)	2·423 ± 0·015		
Na^+–O(*W*)	2·378 ± 0·015		
Na^+–O(4′)	2·455 ± 0·015		
Na^+–O(2′)	2·457 ± 0·015		
Na^+–O(1′)	2·351 ± 0·015		
Na^+–O(*W*′)	2·376 ± 0·015		

tetrahedron. This structure is close to that of tenorite CuO [Fig. 2(*b*)] and is reminiscent of the tetragonal sulphides of palladium and platinum. The structure is stabilized by the hydrogen bonds already mentioned.

The hydrogen-bonded HSO_4^- groups are linked by their acid hydrogen atoms in zigzag chains lying along the mean direction [101], and are cross-linked by water molecules in another chain arrangement along [011]. The mean S–O length is the same as the known length for S–O in SO_4^{2-} measured by Atoji & Rundle (1958), within the standard deviations. This corresponds to the empirical rule proposed by Cruickshank (1961*b*) stating that in XO_4 tetrahedra (X = Si, P, S, Cl) X–O bonds in which the oxygen becomes linked to another atom or to another tetrahedron may lengthen by amounts up to 0·15 Å whilst the other X–O bonds in the tetrahedron contract so as to preserve the average. It is hardly to be expected that this rule could still apply strictly, if most or all of the four oxygen atoms become externally bonded. A formal correlation of various bond lengths is suggested in Fig. 4, in which successive links alternately expand or contract if hypothetically the O–O distance is varied. In this connection we may note first that the S–O(2) bond is longer, having the stronger (2·70 Å) hydrogen bond, than either S–O(1) or S–O(4) in which the oxygen atoms are linked by (2·9 Å) bonds to water molecules. However, whilst this difference appears significant we have not shown the S–O(3)(H) bond to be noticeably shorter than the known S–O(R) bond; if such a difference exists it may be merely obscured by the standard deviations. This is in contrast with Cruickshank's further suggestion that in crystals, when acidic hydrogen is attached to sulphate or phosphate groups, the bonds for S–O(H) and P–O(H) are considerably shorter than when a group R is attached. The difference, attributed to the formation of short hydrogen bonds of 2·49–2·62 Å, is seen in the data of Table 7. As hydrogen bonds become shorter the O–H equilibrium distance becomes more sensitive to changes in the O–H - - - O distance (Fig. 3) (Nakamoto, Margoshes & Rundle, 1955; Pimentel & Sederholm, 1956). Intuitively we should expect the S–O(H) distance to vary accordingly, and to be relatively little influenced by the hydrogen bond if the O–O distance is larger than 2·7 Å, as it is here (larger than in any of the quoted structures).

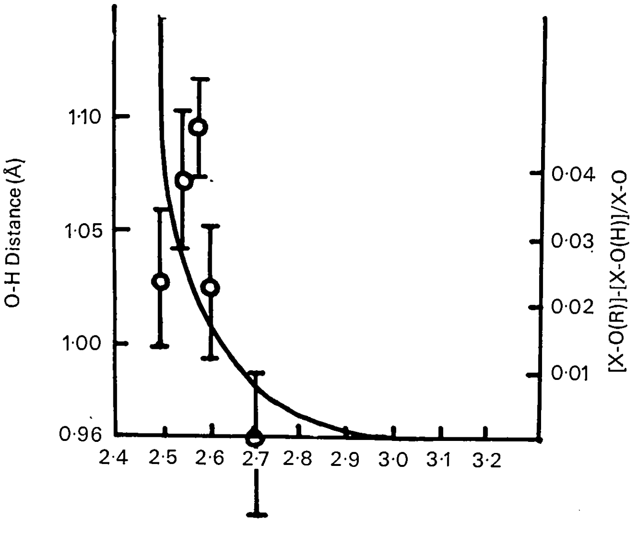

Fig. 3. Superposition of (*a*) curve of O–H distance in hydrogen bond (abscissa: O–O distance) and (*b*) points giving 'shrinkage' of the X–O(H) bond relative to X–O(R)

Table 7. X–O *bond lengths in sulphates and phosphates*

Compound	X–O	X–O(H)	X–O(R)	e.s.d.
$K(C_2H_5)SO_4$	1·46		1·60	± 0·007
$KHSO_4$	1·47	1·56		± 0·015
Serine(HPO_4)	1·50	1·56	1·61	± 0·01
KH_2PO_4	1·51	1·58		± 0·02
H_3PO_4	1·52	1·57		± 0·02

The percentage difference between X–O(R) and X–O(H) is plotted against the O–O hydrogen bond distance also in Fig. 3 for comparison, though the data hardly justify a functional relation. It is clear that on

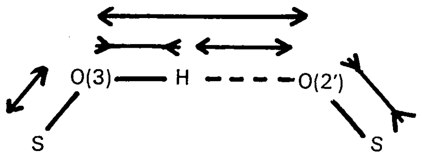

Fig. 4. Suggested correlation of S–O(3) and S–O(2) bond lengths with hydrogen bond length.

this issue we require more data, especially in the form of precisely measured bond lengths.

The structure described above is far from being typically ionic; but it is held together by forces which in their nature and stereochemistry seem to be fully typical of the elements present.

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Structure Cristalline du Bronze de Vanadium-Lithium LiV_2O_5

PAR JEAN GALY ET ANTOINE HARDY

Service de Chimie Minérale (Paul Hagenmuller), Faculté des Sciences de Bordeaux, France

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LiV_2O_5 crystallizes in the orthorhombic system. The space group is $Pna2_1$ (C_{2v}^9), and the parameters are: $a = 9{\cdot}702$, $b = 3{\cdot}607$, $c = 10{\cdot}664$ Å. The structure has been determined by Patterson projections and refined by diagonal approximation. The atoms of oxygen are at the corners of distorted trigonal bipyramids surrounding vanadium atoms. These bipyramids associated in pairs with a common edge form chains parallel to the *Oy* axis. The lithium atoms, surrounded by oxygen atoms at the corners of octahedra, effect the cohesion between these chains.

LiV_2O_5 est la composition limite de la série des bronzes $Li_xV^{4+}_xV^{5+}_{2-x}O_5$ étudiée par Hagenmuller & Lesaicherre (1963). Pour x variant entre 0 et 1, trois phases apparaissent: $Li_xV_2O_5\alpha$ solution solide de lithium dans la maille de V_2O_5 orthorhombique, $Li_xV_2O_5\beta$ monoclinique dont la structure a été décrite précédemment (Galy & Hardy, 1964) et $Li_xV_2O_5\gamma$ orthorhombique dont LiV_2O_5 est la formule limite.

Les cristaux de LiV_2O_5 sont obtenus par fusion sous courant d'argon à 750 °C dans une nacelle de platine, puis refroidissement lent. Ils se présentent sous la forme d'aiguilles prismatiques à base rectangulaire; leur couleur est bleu foncé à reflets métalliques.

L'étude radiocristallographique sur monocristal à été effectuée à l'aide du rayonnement Cu $K\alpha$.

Les données cristallographiques sont rassemblées dans le Tableau 1.

Tableau 1. *Données cristallographiques relatives à* LiV_2O_5

Dimensions de la maille	$a = 9{,}702 \pm 0{,}005$ Å $b = 3{,}607 \pm 0{,}003$ $c = 10{,}664 \pm 0{,}009$
Groupe spatial	$Pna2_1$ ($C_{2v}{}^9$)
D_{obs}	$3{,}35 \pm 0{,}05$
D_{calc}	3,38
Nombre de motifs par maille	$Z = 4$

Les paramètres ont été précisés par la méthode du cristal oscillant. Le groupe d'espace a été déterminé à l'aide du rétigraphe Rimsky pour les plans *h*0*l*, *h*1*l*, *h*2*l*, *h*3*l*. Il a été confirmé par l'étude des plans réticulaires suivant les deux autres directions sur le goniomètre de précession de Buerger.

La mesure de l'intensité des taches sur les rétigrammes relatifs aux plans *h*0*l*, *h*1*l*, *h*2*l*, *h*3*l* a été faite avec le microdensitomètre Vassy MD3.