CROSBY, B. L. & KIRK, P. L. (1935). *Mikrochemie*, **18**, 137.
CRUICKSHANK, D. W. J., PILLING, D. E., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis.* Edited by R. PEPINSKY, J. M. ROBERTSON & J. C. SPEAKMAN. p. 32. New York: Pergamon Press.
CRUICKSHANK, D. W. J. & MCDONALD, W. S. (1967). *Acta Cryst.* **23**, 9.
DEXTER, D. D. (1972). *Z. Kristallogr.* In the press.
HUBER, C. S. (1969). *Acta Cryst.* B**25**, 1140.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
IUPAC–IUB COMMISSION ON BIOCHEMICAL NOMENCLATURE (1970). *J. Mol. Biol.* **52**, 1.
LOW, B. W. & RICHARDS, F. M. (1952). *J. Amer. Chem. Soc.* **74**, 1660.
MARSH, R. E. & DONOHUE, J. (1967). Chapter in *Advanc. Protein. Chem.* p. 22. New York: Academic Press.
MARSH, R. E. & GLUSKER, J. P. (1961). *Acta Cryst.* **14**, 1110.
STEIN, W. H., MOORE, S. & BERGMAN, M. (1944). *J. Biol. Chem.* **154**, 191.
STEWART, J. M. (1970). *Crystallographic Computing.* Edited by F. R. AHMED, p. 71. Copenhagen: Munksgaard.
STEWART, J. M. (1967). X-ray 67 Program System for X-ray Crystallography, Technical Report 67–58, Computer Center, Univ. of Maryland.
STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination.* p.422. New York: Macmillan.

Acta Cryst. (1972). B**28**, 3559

The Crystal Structure of Sborgite, $NaB_5O_6(OH)_4.3H_2O$

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The crystal structure of sborgite (space group $C2/c$, cell parameters $a = 11{\cdot}119$, $b = 16{\cdot}474$, $c = 13{\cdot}576$ Å, $\beta = 112°50'$) was determined by the symbolic addition method and refined by the least-squares method (with anisotropic thermal parameters for non-hydrogen atoms) to a final R value of 0.062. The structure contains the pentaborate ion $[B_5O_6(OH)_4]^-$ characterized by the double ring built up from one BO_4 tetrahedron and three BO_3 triangles. The two sodium ions in the asymmetric unit are in special positions along a binary axis: one is octahedrally coordinated by four water molecules and two hydroxyl ions, the other is tetrahedrally coordinated by two water molecules and two hydroxyl ions, with two more distant contacts at nearly 3 Å. A complex system of hydrogen bonds connects the pentaborate ions and the sodium coordination polyhedra.

Introduction

Sborgite was reported as a new mineral phase by Cipriani (1957) who found it associated with borax and thenardite among the compounds incrusting the training pipes of some 'soffioni' in the boriferous area of Larderello. Cipriani identified it, on the basis of its powder diffraction pattern, optical data and density, with the compound $NaB_5O_8.5H_2O$, synthesized and studied by Sborgi in his researches on the ternary system Na_2O–B_2O_3–H_2O. The cell data and space group were determined by Sabelli (1962).

Christ (1960), in his study on the crystal chemistry of hydrated borates, advanced the hypothesis that sborgite must contain the pentaborate ion $[B_5O_6(OH)_4]^-$, known to exist, to that date, in the compound $NH_4B_5O_6(OH)_4.2H_2O$ and in its potassium analogue $KB_5O_6(OH)_4.2H_2O$ (Zachariasen, 1937). Recently we found this same group isolated, or variously polymerized, in some minerals and artificial products (Merlino, 1969; Merlino & Sartori, 1969, 1971). We were thus strongly motivated to undertake the structural study of sborgite in order to define its position in the crystal-chemical classification of borates and its relations with the other compounds containing the pentaborate group.

Experimental

Synthetic crystals of sborgite, suitable for X-ray single-crystal investigations, were obtained following the suggestions of Cipriani (1957). Unit-cell constants were determined from the least-squares refinement of powder data.

Sborgite, $NaB_5O_8.5H_2O$ M.W. 295·17
Monoclinic, space group $C2/c$ or Cc ($C2/c$ established by intensity statistics)

$a = 11{\cdot}119$ (8) Å
$b = 16{\cdot}474$ (14)
$c = 13{\cdot}576$ (9)
$\beta = 112°50$ (2)$'$

Unit-cell volume, $V = 2291{\cdot}9$ Å^3 $Z = 8$
$D_m = 1{\cdot}713$ g.cm^{-3}, as determined by Sabelli, $D_c = 1{\cdot}711$ g.cm^{-3}, $F(000) = 1200$, $\mu = 17{\cdot}0$ cm^{-1} (Cu $K\alpha$).

The intensity data were recorded with nickel-filtered Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å), by means of Weissenberg photographs, with the multiple-film technique and integration process. A fragment elongated in the **a** direction was cut from a large crystal and reduced to cylindrical shape with cross sectional radius of 0·025 cm ($\mu R = 0{\cdot}382$ for Cu $K\alpha$ radiation). Eleven layers with a as rotation axis ($h = 0$ through 10) were recorded and 2274 independent reflexions (1618 observed) were collected. The intensities, measured with a Nonius microdensitometer, have been corrected for Lorentz and polarization factors, for incipient but incomplete α_1–α_2 spot doubling and for the absorption factor: the last correction was performed by the three-constants formula proposed by Palm (1964) for cylindrical crystals.

By means of the *DATFIX* program, incorporated in the Crystal Structures Calculations System X-ray 70 (Stewart, 1970), an overall isotropic temperature factor, the scale factors and the normalized structure-factor magnitudes E were calculated. The method of calculation of the estimated parameters is based upon the normal statistics of the E magnitudes. The statistical averages and distribution of E are given in Table 1, compared with the theoretical values for both a centrosymmetric and a non-centrosymmetric distribution of atoms in the unit cell. The unobserved reflexions were given an intensity of one half the minimum observed value. There is clear evidence for accepting the space group as $C2/c$.

Table 1. *Statistical averages and distributions of* $|E|$.

	Experimental	Centro-symmetric	Non-centro-symmetric
$\langle\lvert E\rvert\rangle$	0·812	0·798	0·886
$\langle\lvert E^2-1\rvert\rangle$	0·946	0·968	0·736
$\langle\lvert E^2\rvert\rangle$	1·000	1·000	1·000
$\lvert E\rvert>3$	0·003	0·003	0·0001
$\lvert E\rvert>2$	0·038	0·045	0·018
$\lvert E\rvert>1$	0·322	0·317	0·368

Structure determination and refinement

The structure was solved by obtaining the values of the phases directly from the normalized structure-factor magnitudes by means of the symbolic addition procedure. The origin of the unit cell was fixed by assigning phases to two reflexions with permitted parities; one additional sign was assigned to the reflexion 0,10,0 on the basis of the $\sum_1$ relation. Symbols a through f were assigned to six additional reflexions, introduced as necessary during the development of the phase determination. Sign and symbol assignments are shown in Table 2.

Table 2. *Signs and symbols used in the application of the* $\sum_2$ *relationships*

h	k	l	E	Sign or symbol
1	1	15	3·20	+
3	3	$\bar{6}$	2·78	+
0	10	0	2·07	−
5	9	$\overline{10}$	2·93	a
5	5	7	3·31	b
0	4	10	2·74	c
1	1	11	2·50	d
6	8	$\bar{8}$	2·78	e
1	5	$\overline{13}$	3·23	f

The application of the method was facilitated by the preparation of lists of the reflexion combinations in the $\sum_2$ formula, by means of the *SIGMA* 2 program in the X-ray 70 System (Stewart, 1970). Signs and symbols were derived by hand application of the $\sum_2$ formula for the eighty reflexions with $E\geq 2{\cdot}0$. Several relations among the symbols a through f were obtained and the least number of discrepancies among sign indications corresponded to the following solution for symbols: $a=+$, $b=-$, $c=+$, $d=+$, $e=+$, $f=-$. In the preceding step, symbol indications were accepted only if the probability was not less than 0·97. The sign determination was then extended to all the reflexions with $E\geq 1{\cdot}5$ by automatic application of the $\sum_2$ formula by means of the *PHASE* program in the X-Ray 70 System (Stewart, 1970).

A three-dimensional E map, calculated with the contribution of 260 of the largest E's, clearly showed

Table 3. *Observed and calculated structure factors* $(\times 10^2)$

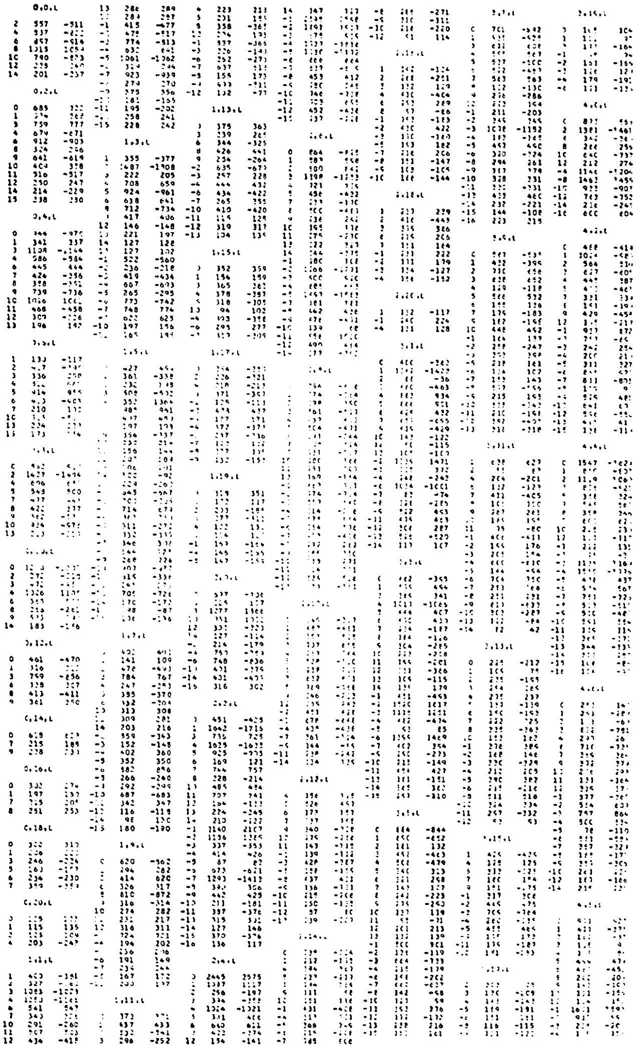


Table 3 (*cont.*)

4,5,L		
-5	343	-357
-6	243	-273
-7	516	-532
-8	423	471
-9	233	216
-10	226	-237
-11	271	-294
-14	193	187
-15	171	-169
-16	124	-79
4,10,L		
0	436	-397
2	395	393
3	204	-177
5	359	-362
6	121	-131
7	189	-179
10	236	239
-2	88	-87
-3	336	-329
-5	150	146
-7	381	373
-8	865	-900
-9	565	542
-10	201	192
-12	255	257
-13	379	376
-14	111	92
-15	124	-123
4,12,L		
1	227	224
2	294	-269
4	163	-131
5	156	-147
7	392	-410
8	132	-119
9	265	296
-1	233	-237
-2	424	404
-3	472	-477
-5	230	166
-7	342	328
-8	366	-374
-9	274	247
-10	241	232
-11	244	293
-12	204	203
-14	233	224
4,14,L		
0	472	-422
1	676	676
2	723	-727
3	472	465
4	137	147
5	122	-133
9	133	-131
-2	144	135
-3	420	-447
-6	304	-233
-9	174	197
-11	290	-280
-12	47	-92
4,16,L		
0	139	-120
1	142	-120
4	140	133
5	223	210
6	175	174
7	118	-123
-1	249	245
-3	233	-252
-5	133	-187
-7	126	-122
-8	141	159
-9	220	225
-11	119	-147
4,18,L		
0	135	-137
2	83	80
-1	179	-193
-4	90	103
-5	139	149
-8	130	120
-9	61	-87
5,1,L		
1	782	-784
2	776	-717
4	420	-411
5	174	-147
6	174	149
7	351	309
8	314	327
9	274	-267
10	197	-210
11	59	-101
12	134	96
-1	1047	1125
-2	463	457
-3	155	-232
-5	93	127
-6	303	306
-7	143	-137
-9	134	-129
-10	341	342
-12	711	-719
-13	424	-417
-14	223	221
-15	272	255
-17	230	192
5,3,L		
0	266	193
1	244	254
2	294	262
3	459	349
4	614	591
5	228	214
6	229	-210
7	444	476
8	349	378
9	134	-123
-1	283	-233
-2	437	419
-3	145	-127
-4	490	509
-5	167	142
-6	816	-851
-7	448	-423
-8	347	-334
-9	333	-304
-10	335	330
-11	451	-426
-12	628	623
-15	176	186
-17	217	-226
5,5,L		
0	302	284
1	830	-784
2	653	-618
3	483	469
4	593	573
5	931	942
6	582	-558
7	726	-771
8	284	325
9	159	-162
10	176	-191
12	219	-219
-1	352	-373
-2	707	-748
-3	1439	1471
-4	532	525
-5	148	100
-6	629	-639
-7	513	-517
-8	169	196
-9	145	-133
-10	611	621
-11	230	181
-13	160	-120
-14	87	-97
5,7,L		
0	127	127
1	394	396
2	165	-153
3	170	177
4	131	-153
7	358	-340
8	209	225
9	338	-268
10	131	-136
11	72	-63
-1	113	-84
-2	328	320
-3	495	491
-4	97	-67
-5	553	554
-6	567	583
-7	332	-320
-8	522	497
-9	227	-226
-10	165	-105
-11	107	-81
-12	131	-113
-13	291	291
-14	259	229
-16	330	-271
5,9,L		
0	754	-701
1	132	-120
2	175	154
3	215	-189
4	223	233
6	188	-171
7	217	203
8	342	-352
9	133	-154
10	138	176
11	88	109
-1	409	409
-2	205	-230
-3	465	-453
-4	420	-397
-5	247	223
-7	258	-242
-8	427	-442
-9	256	-234
-10	994	964
-11	372	-359
-12	132	99
-14	453	435
5,11,L		
1	127	-134
2	330	307
3	347	-333
4	307	-271
5	261	-258
7	88	-119
8	166	140
9	169	161
10	114	-132
-1	563	-551
-2	163	-147
-3	424	-436
-4	279	264
-5	348	-348
-7	424	412
-9	194	191
-13	111	73
-14	95	-132
5,13,L		
0	473	473
4	403	407
5	231	93
6	251	-255
7	233	-215
8	244	253
-1	171	-203
-2	558	-576
-4	527	626
-5	241	-236
-6	139	-82
-7	139	-149
-8	114	137
-10	303	-313
-11	234	-256
-12	151	-127
-13	122	-117
5,15,L		
0	129	-97
1	124	140
2	197	163
4	52	-32
5	134	-127
7	80	-72
-1	264	256
-4	382	-403
-3	113	137
-7	103	111
-8	104	89
-11	290	-252
-12	134	-112
5,17,L		
0	213	-219
2	137	145
3	112	-120
5	117	131
-1	110	-57
-2	246	269
-3	147	146
-6	103	73
-7	119	130
-8	127	-124
-9	236	177
-10	241	307
5,19,L		
0	99	175
-5	103	-77
6,0,L		
0	715	721
2	348	342
4	439	421
6	533	-603
8	175	201
10	416	-452
-4	395	-375
-6	1254	-1351
-8	1419	1462
-12	414	389
-14	154	-142
-16	285	267
6,2,L		
0	632	562
1	213	-202
2	485	465
3	322	307
4	458	471
5	164	156
6	445	-466
7	322	274
8	136	-109
10	165	179
11	199	-187
-1	330	-293
-2	406	-367
-3	535	-610
-4	138	154
-5	636	733
-6	158	-122
-7	196	37
-8	94	43
-10	525	534
-11	425	-426
-12	218	-171
-13	160	129
-14	243	-226
-15	257	-271
-17	343	347
6,4,L		
2	549	-534
4	672	-693
5	576	377
7	311	-302
8	201	-197
9	208	-185
11	132	-119
-1	422	-347
-2	610	574
-3	130	159
-4	200	-221
-5	750	-731
-6	135	230
-7	174	135
-8	350	331
-9	113	-109
-10	239	252
-12	531	-563
-13	311	-252
-14	167	295
-15	124	-114
-17	147	123
6,6,L		
0	201	152
3	211	-212
4	356	345
5	249	229
6	127	-131
7	128	-136
8	172	165
9	221	-225
-1	507	-442
-2	444	-459
-3	473	465
-4	666	666
-6	192	167
-7	476	417
-8	460	-407
-9	446	418
-10	248	-241
-11	337	322
-12	245	234
-13	156	-134
-14	200	-220
6,8,L		
1	122	-118
2	260	-237
3	204	122
4	228	176
5	172	-142
6	120	106
7	154	124
8	171	401
9	211	216
-1	149	132
-2	139	-142
-3	287	-318
-4	726	677
-5	401	-358
-7	222	-218
-10	187	[illegible]
-12	214	193
-13	298	-230
-15	146	103
6,10,L		
1	254	-264
2	515	500
3	419	-442
4	120	-134
5	126	-91
6	107	122
8	157	117
-1	149	159
-2	146	54
-4	623	629
-5	154	-152
-7	400	-408
-8	151	138
-11	159	-150
-14	130	119
6,12,L		
2	706	778
3	154	-135
5	117	120
6	117	139
7	149	-133
8	164	145
-1	474	415
-2	261	222
-3	510	513
-4	912	900
-5	196	-211
-12	232	-234
-13	190	-197
6,14,L		
1	141	158
2	160	145
3	153	-149
5	168	-164
6	113	-126
-2	175	-161
-3	115	-115
-4	208	210
-10	207	212
6,16,L		
1	146	132
2	98	-31
3	162	-215
-6	195	-149
-7	191	167
-8	86	71
-9	113	-104
-10	124	214
6,18,L		
1	53	18
-2	159	-168
-3	118	129
-5	55	-63
-6	252	-264
7,1,L		
0	433	405
1	304	-310
2	270	-233
3	305	634
5	139	131
7	201	-212
9	259	248
5	83	-56
-1	353	-343
-2	366	-358
-3	338	333
-4	114	122
-5	231	245
-6	256	-233
-7	116	106
-8	85	-98
-9	110	159
-11	562	552
-12	395	349
-13	249	-223
-14	457	-506
-15	323	-327
7,3,L		
0	155	-165
1	194	190
2	237	-239
4	620	-617
5	242	218
6	511	533
7	288	-237
10	104	58
-1	645	-606
-2	219	236
-3	166	158
-4	198	-55
-5	460	545
-7	165	-142
-8	432	450
-9	540	-557
-10	138	116
-11	262	229
-12	342	-329
-13	258	-266
-14	245	-229
-16	112	-73
-17	167	-66
7,5,L		
1	336	-329
2	149	-119
3	167	-141
4	283	-283
5	260	359
7	192	149
8	240	-261
10	57	-55
-1	436	357
-2	257	-239
-3	601	616
-4	237	274
-5	111	-113
-6	169	155
-8	513	-515
-10	301	305
-11	418	-416
-12	331	362
-15	165	97
-16	283	278
7,7,L		
0	452	482
1	282	-283
2	513	570
3	169	141
4	155	143
7	282	283
8	135	143
-2	442	-423
-3	401	-386
-4	666	661
-5	363	358
-6	522	-538
-7	158	-157
-8	244	-243
-10	346	-344
-11	189	-187
-12	226	248
-13	338	323
-16	137	85
7,9,L		
1	169	-392
2	331	324
3	282	270
4	53	87
5	56	-78
6	137	-150
7	146	-145
8	118	-116
-1	552	-519
-2	129	-125
-3	437	456
-4	283	383
-5	215	-183
-6	593	575
-7	351	-223
-8	288	-237
-10	340	-168
-11	345	376
-12	117	143
7,11,L		
1	335	368
2	231	155
3	215	-281
4	141	-121
6	111	113
7	193	-113
-1	116	117
-2	153	-137
-3	682	689
-4	300	-120
-5	264	-164
-7	465	470
-8	156	150
-9	242	-251
-10	233	-216
-11	132	152
-13	195	-191
-14	181	151
7,13,L		
1	151	-127
3	130	-189
4	133	160
6	188	-201
-1	101	56
-2	250	-243
-3	209	-175
-5	273	-255
-6	151	-148
-8	93	-105
-9	170	159
-12	298	294
7,15,L		
2	81	-90
3	232	239
4	224	-228
-3	344	-357
-8	124	112
-9	96	95
-11	84	75
7,17,L		
1	188	175
2	56	114
-1	116	-121
-3	142	130
-5	65	-84
-6	81	72
-8	123	-109
8,0,L		
2	309	-311
4	728	-789
6	267	296
-6	97	-147
-5	375	320
-12	237	244
-16	283	240
8,2,L		
1	154	-301
2	329	291
3	594	541
4	153	-172
5	423	-423
7	217	-159
9	244	-250
-1	620	167
-2	338	294
-3	166	-156
-4	119	-219
-5	382	426
-6	99	84
-7	665	-681
-8	556	-570
-10	213	-204
-11	259	249
-12	315	294
-13	205	201
-14	234	-231
-15	235	-219
-17	136	141
8,4,L		
1	403	372
2	294	205
3	134	149
4	166	-153
5	227	-217
6	297	272
7	59	-71
8	193	-173
9	166	-166
-1	374	-322
-2	100	-31
-3	230	-215
-4	185	-199
-5	288	-310
-6	133	-120
-7	112	120
-9	200	189
-11	418	409
-14	141	143
-16	116	68
8,6,L		
0	553	-527
1	887	915
4	109	107
5	196	197
6	169	-177
7	116	-123
-1	181	159
-2	379	-412
-3	110	-100
-4	273	274
-5	309	-256
-7	491	490
-9	289	-236
-10	232	-251
-11	282	284
-12	298	292
-13	383	-350
-14	122	-102
-16	298	261
8,8,L		
0	247	-227
1	380	-371
2	145	139
3	225	194
4	214	-164
5	157	-193
6	215	231
7	154	-187
-1	279	253
-2	290	-275
-3	176	177
-4	454	-476
-6	364	387
-7	250	-280
-8	251	307
-9	318	303
-10	195	-201
-12	177	-155
8,10,L		
0	188	-164
1	309	-253
2	367	405
4	139	-107
5	133	-154
6	135	141
7	63	95
-1	159	135
-2	201	-196
-3	315	-291
-4	149	-57
-5	241	195
-6	635	651
-7	132	-177
-11	120	-101
-12	142	14
8,12,L		
0	168	74
2	115	-75
3	43	-101
4	110	117
5	142	-185
-1	238	-203
-2	144	-154
-4	163	-127
-7	243	205
-8	170	-147
-9	246	-252
-11	55	-74
-12	111	134
8,14,L		
2	42	81
3	133	-116
-4	202	181
-5	120	143
-6	161	-173
-7	46	87
-9	210	-187
-10	156	161
8,16,L		
0	128	132
1	144	-133
-2	300	342
-3	145	133
-6	209	-195
-8	145	-103
-9	83	75
9,1,L		
1	309	-307
2	306	-277
4	326	-309
6	228	235
7	204	187
9	75	76
-1	287	255
-2	267	243
-3	365	369
-4	302	-327
-5	159	-213
-7	225	-236
-8	176	197
-9	132	156
-10	616	599
-11	511	-505
-12	234	209
-13	162	-141
9,3,L		
0	227	229
1	380	-328
2	236	192
3	123	-117
4	220	-210
6	242	253
8	72	-77
-2	345	337
-3	309	-309
-4	325	-397
-5	61	-65
-6	174	-171
-8	515	-527
-9	122	-64
-15	172	139
9,5,L		
0	125	87
1	121	-124
2	116	156
3	201	201
7	75	-72
-1	768	-734
-2	202	219
-3	251	253
-6	325	356
-7	315	-318
-10	214	-259
-11	437	476
9,5,L		
-12	215	201
-14	220	-247
-15	297	-275
-16	124	-131
9,7,L		
1	230	-203
2	170	-151
-1	234	277
-2	352	-345
-4	306	-324
-5	477	439
-6	244	205
-7	125	-73
-8	137	143
-10	175	-172
-12	246	-239
-15	226	-204
9,9,L		
0	153	-136
1	363	-377
2	319	325
3	143	-124
5	137	157
-1	333	351
-2	144	135
-3	126	107
-4	288	-309
-5	447	424
-7	171	-140
-8	226	-219
-9	195	171
-10	144	-132
-14	194	158
9,11,L		
1	301	301
4	137	-132
5	90	125
-1	133	-135
-3	221	-215
-4	180	202
-5	134	-113
-9	254	-229
-12	184	148
-13	159	-137
9,13,L		
0	105	-76
-2	165	-175
-4	233	224
-5	160	172
-6	131	126
-7	74	-114
-10	133	-124
-12	43	43
9,15,L		
0	76	57
-4	243	247
-6	94	53
-7	136	-51
-9	143	165
10,0,L		
0	123	66
2	553	-534
4	437	505
6	131	67
-4	287	300
-6	201	-133
-8	131	145
-10	267	-245
-12	164	-172
-14	145	-123
-16	149	154
10,2,L		
0	187	-163
1	224	155
2	178	-140
5	167	150
6	49	68
-1	612	610
-2	67	62
-3	264	-317
-5	80	-70
-6	109	102
-7	118	15
-8	133	-124
-9	192	-210
-10	169	-157
-11	424	-411
-14	174	167
-15	170	-166
10,4,L		
2	124	-110
3	108	-107
4	129	-153
6	201	215
-1	130	113
-2	188	136
-3	507	441
-4	435	-365
-6	603	651
-7	214	-294
-8	236	-155
-10	267	239
-11	237	244
-12	331	-355
-13	111	100
-14	186	251
10,6,L		
0	254	297
1	195	-132
2	144	149
3	195	167
4	68	131
5	203	-170
-2	190	-59
-5	182	125
-6	265	268
-7	257	-389
-8	148	157
-9	228	-240
-11	202	206
-12	264	239
-13	96	-63
10,8,L		
0	257	275
4	241	221
5	125	-149
-2	181	-139
-3	142	-159
-4	215	-239
-5	252	273
-6	234	-229
-7	109	-104
-8	42	116
-9	210	-131
-11	175	-169
-12	147	121
-13	155	150
10,10,L		
1	182	143
2	167	139
3	136	-106
-2	102	69
-3	239	-229
-4	192	-165
-7	156	209
-8	115	-121
-10	144	123
-11	164	-119
-13	129	-103
10,12,L		
-1	233	-236
-2	137	13
-3	141	115
-4	207	-274
-5	273	203
-10	136	-91
10,14,L		
-2	367	-417
-5	156	165
-7	134	157
-8	33	-87
-9	54	6

the positions of all the heavy atoms in the structure. The coordinates of the heavy atoms as read from the E map were then refined by the full-matrix least-squares program *ORFLS* of Busing, Martin & Levy (1962) in the X-ray 70 System (Stewart, 1970). Individual scale factors for each layer were varied during the refinement; their starting values were those obtained by the *DATFIX* program. After three refinement cycles with isotropic temperature factors the value of the reliability index, defined as $R_1=\sum||F_o|-|F_c||/\sum|F_o|$, was 0·11.

Refinement was continued with anisotropic temperature factors in the forms:

$$\exp\{-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\}\,.$$

The restrictions on the thermal ellipsoids of the two sodium atoms in special positions on the twofold axis are that $\beta_{12}=\beta_{23}=0$ (Levy, 1956). Because of the degeneracy between β_{11} and the scale factors (Lingafelter & Donohue, 1966), the latter were rescaled after each cycle but not refined in the least-squares process. A refinement cycle reduced the reliability index to $R_1=0{\cdot}073$.

A three-dimensional difference Fourier synthesis calculated at this stage revealed generally well defined peaks in positions where hydrogen atoms were expected on the basis of stereochemical considerations. The hydrogen atoms were included in the structure-factor calculations with isotropic temperature factors $B=5{\cdot}0$ Å^2. After two refinement cycles in which the parameters of the hydrogen atoms were not refined, the reliability index decreased to $R_1=0{\cdot}062$, whereas $R_2=[\sum w||F_o|-|F_c||^2/\sum w|F_o|^2]^{1/2}$ was 0·063. Unit weights were assigned initially, but at the beginning of the anisotropic refinement the following weighting scheme, based on the plot of ΔF *vs.* F_o, was introduced:

$w=0$ for unobserved reflexions

$$\sqrt{w}=\frac{F_o}{50{\cdot}0}\text{ for }F_o\le 50{\cdot}0$$

$$\sqrt{w}=\frac{50{\cdot}0}{F_o}\text{ for }F_o>50{\cdot}0$$

The reflexion $60\bar{2}$ was excluded from the refinement, being too strong on the last film.

The shifts of all the parameters in the last cycle were well within their standard deviations, with an average $\Delta/\sigma=0{\cdot}4$, Δ being the change in a parameter in the last least-squares cycle and σ the e.s.d. of the parameter in that cycle.

The scattering factors used in the structure-factor calculations were taken from *International Tables for X-ray Crystallography* (1962). The observed and calculated factors are compared in Table 3. Table 4 gives the final positional and thermal parameters of all the atoms with their standard deviations.

Description and discussion of the structure

The principal structural features of sborgite are illustrated in Fig. 1, in which the structure is described in terms of boron coordination triangles and tetrahedra. Assignment of the hydrogen atoms can be made assuming, according to Christ's (1960) third rule, that the oxygen atoms O(1), O(3), O(8) and O(10), not shared between two boron atoms in the pentaborate ion, represent hydroxyl groups, and that the three unattached oxygen atoms O(11), O(12) and O(13)

Table 4. *Positional and thermal parameters for heavy atoms and positional parameters for hydrogen atoms*

Standard deviations are given in parentheses. Values for the heavy atoms are multiplied by 10^4 and for the hydrogen atoms by 10^3.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Na(1)	0	1528 (2)	2500	44 (3)	20 (1)	26 (2)	0	10 (2)	0
Na(2)	5000	1228 (2)	2500	185 (6)	23 (1)	34 (2)	0	56 (3)	0
O(1)	4038 (4)	2925 (2)	259 (3)	73 (4)	29 (2)	25 (2)	14 (2)	18 (2)	1 (1)
O(2)	2264 (3)	3827 (2)	−384 (2)	69 (4)	26 (2)	17 (2)	12 (2)	12 (2)	3 (1)
O(3)	413 (3)	4635 (2)	−1098 (2)	79 (4)	34 (2)	10 (2)	22 (2)	−9 (2)	2 (1)
O(4)	3281 (3)	3561 (2)	1487 (2)	52 (4)	21 (1)	19 (2)	6 (2)	8 (2)	2 (1)
O(5)	1406 (3)	4448 (2)	798 (2)	42 (4)	22 (1)	15 (2)	8 (2)	3 (2)	−1 (1)
O(6)	1979 (3)	3784 (2)	2491 (2)	49 (4)	20 (1)	16 (2)	−8 (2)	3 (2)	−5 (1)
O(7)	3291 (3)	4874 (2)	2278 (2)	54 (4)	18 (1)	13 (2)	−10 (2)	2 (2)	−1 (1)
O(8)	2189 (3)	3449 (2)	4259 (2)	73 (4)	32 (2)	22 (2)	−21 (2)	15 (2)	1 (1)
O(9)	3612 (3)	4403 (2)	4018 (2)	43 (4)	20 (1)	17 (2)	−15 (2)	2 (2)	0 (1)
O(10)	4750 (3)	5562 (2)	3755 (2)	59 (4)	21 (1)	24 (2)	−18 (2)	9 (2)	−1 (1)
O(11)	158 (3)	2609 (2)	1386 (2)	42 (4)	23 (1)	31 (2)	−4 (2)	13 (2)	−4 (1)
O(12)	2278 (3)	1422 (2)	3588 (3)	55 (4)	20 (1)	34 (2)	−4 (2)	8 (2)	−4 (1)
O(13)	3998 (3)	2271 (2)	3014 (3)	64 (4)	29 (2)	33 (2)	−1 (2)	15 (3)	4 (2)
B(1)	2500 (5)	4161 (3)	1769 (4)	42 (7)	21 (2)	9 (3)	1 (3)	0 (3)	3 (2)
B(2)	3212 (6)	3433 (4)	480 (4)	37 (6)	17 (2)	34 (3)	3 (3)	19 (4)	−1 (2)
B(3)	1387 (6)	4310 (4)	−189 (4)	43 (7)	20 (2)	22 (3)	1 (3)	8 (4)	4 (2)
B(4)	2552 (6)	3863 (4)	3571 (4)	58 (7)	17 (2)	17 (3)	−2 (3)	12 (3)	−2 (2)
B(5)	3867 (5)	4940 (3)	3358 (4)	41 (6)	18 (2)	16 (3)	−3 (3)	5 (3)	−3 (2)

Table 4 (*cont.*)

H(1)	477	267	89
H(3)	−18	490	−81
H(8)	121	316	400
H(10)	485	556	453
H(111)	91	301	162
H(112)	36	240	74
H(121)	236	149	436
H(122)	242	77	353
H(131)	379	268	250
H(132)	327	215	327

represent water molecules: these assignments were confirmed by the difference Fourier synthesis. The structure can thus be described as made up of pentaborate ions linked to each other either directly through hydrogen bonds or through sodium ions and water molecules.

Pentaborate group

The pentaborate ion, characterized by the double ring built up from one BO_4 tetrahedron and three BO_3 triangles, was first found by Zachariasen (1937) in $KB_5O_6(OH)_4.2H_2O$ and is also present in its ammonium analogue $NH_4B_5O_6(OH)_4.2H_2O$. More recently it was also found in β-$NH_4B_5O_6(OH)_4.2H_2O$ (Merlino, 1969).

Bond lengths and angles in the pentaborate group are reported in Table 5 and Fig. 2. The average B–O distance in the triangles is 1·361 Å and in the tetrahedron 1·468 Å, in good agreement with the results previously found in other borates by various workers. In Table 6 the average boron-oxygen bond lengths in sborgite are compared with the corresponding values found in $KB_5O_6(OH)_4.2H_2O$ (Zachariasen & Plettinger, 1963) and in β-$NH_4B_5O_6(OH)_4.2H_2O$. In this Table O^b and O^{nb} represent respectively oxygen atoms linked to two boron atoms in the trigonal state (bridging oxygen atoms), and oxygen atoms linked to only one boron in the trigonal state (non-bridging oxygen atoms). The average B–O^b and B–O^{nb} distances are appreciably different in all three compounds. Coulson (1964, 1969) and Coulson & Dingle (1968) explain the difference of bond lengths of trigonal B–O bonds in terms of differences in π-bond order, which should clearly be smaller for a B–O^b bond than for a B–O^{nb} bond: Coulson & Dingle (1968), using the simple Hückel theory, obtained π-bond orders of 0·447 and 0·512 for B–O^b and B–O^{nb} respectively. On the other hand Zachariasen (1963) used Pauling's valence neutralization concept to explain the variations in B–O bond lengths. In fact in the case of sborgite two B–O^{nb} bonds, that is B(3)–O(3) (1·393 Å) and B(5)–O(10) (1·376 Å) are longer than the adjacent B–O^b bonds, that is B(3)–O(2) (1·362 Å) and B(5)–O(9) (1·364 Å).

Table 5. *Bond lengths and angles in the pentaborate group*

E.s.d.'s are given in parentheses.

Triangularly coordinated boron			
Distance		Angle	
B(2)–O(1)	1·359 (8) Å	O(1)–B(2)–O(2)	117·2 (5)°
B(2)–O(2)	1·395 (6)	O(1)–B(2)–O(4)	122·6 (4)
B(2)–C(4)	1·356 (7)	O(2)–B(2)–O(4)	120·2 (5)
B(3)–O(2)	1·362 (8)	O(2)–B(3)–O(3)	114·9 (5)
B(3)–O(3)	1·393 (6)	O(2)–B(3)–O(5)	123·6 (4)
B(3)–O(5)	1·352 (7)	O(3)–B(3)–O(5)	121·4 (5)
B(4)–O(6)	1·360 (6)	O(6)–B(4)–O(8)	124·2 (5)
B(4)–O(8)	1·339 (7)	O(6)–B(4)–O(9)	119·2 (5)
B(4)–O(9)	1·412 (6)	O(8)–B(4)–O(9)	116·6 (4)
B(5)–O(7)	1·357 (6)	O(7)–B(5)–O(9)	121·8 (4)
B(5)–O(9)	1·364 (7)	O(7)–B(5)–O(10)	116·6 (5)
B(5)–O(10)	1·376 (6)	O(9)–B(5)–O(10)	121·6 (4)
Tetrahedrally coordinated boron			
B(1)–O(4)	1·462 (7) Å	O(4)–B(1)–O(5)	110·4 (4)°
B(1)–O(5)	1·482 (5)	O(4)–B(1)–O(6)	108·7 (4)
B(1)–O(6)	1·456 (7)	O(4)–B(1)–O(7)	110·8 (4)
B(1)–O(7)	1·470 (6)	O(5)–B(1)–O(6)	109·3 (4)
		O(5)–B(1)–O(7)	107·3 (4)
		O(6)–B(1)–O(7)	110·2 (4)

Table 6. *Average boron–oxygen bond lengths in sborgite,* $KB_5O_6(OH)_4.2H_2O$ *and* β-$NH_4B_5O_6(OH)_4.2H_2O$

Compound	Triangle B–O^b	B–O^{nb}	Tetrahedron
$NaB_5O_6(OH)_4.3H_2O$	1·383 Å	1·361 Å	1·468 Å
$KB_5O_6(OH)_4.2H_2O$	1·372	1·352	1·478
β-$NH_4B_5O_6(OH)_4.2H_2O$	1·379	1·356	1·479

The differences in bond lengths are opposite to those calculated discussing only the molecular structure of the pentaborate ion, as in the case of the Coulson & Dingle treatment. These differences are explained by taking into account the crystal packing effect, as in the Pauling–Zachariasen method of the balancing of valences. The lengthening of B(3)–O(3) and B(5)–O(10) bonds relative to the other B–O^{nb} bonds is then related to Na–O bonds which O(3) and O(10) make with Na(2) and Na(1) respectively (for the balance of valences see below). Thus the situation is very similar to that found in the field of silicate structures where the variations in the Si–O distances can be explained in terms of *d–p* π-bonding as suggested by Cruickshank (1961), or on the basis of the Pauling–Zachariasen method of the balancing of valences. However for both Si–O bonds and trigonal B–O bonds the two theories are not necessarily exclusive and we can say, in accordance with Pant (1968), that π-bonding in trigonal B–O bonds 'may be part of the mechanism whereby valency balance is achieved'.

The least-squares planes for the B_2O_5 groups formed by the coordination triangles are given in Table 7. The planes of the two B_2O_5 groups make an angle of 87·1°.

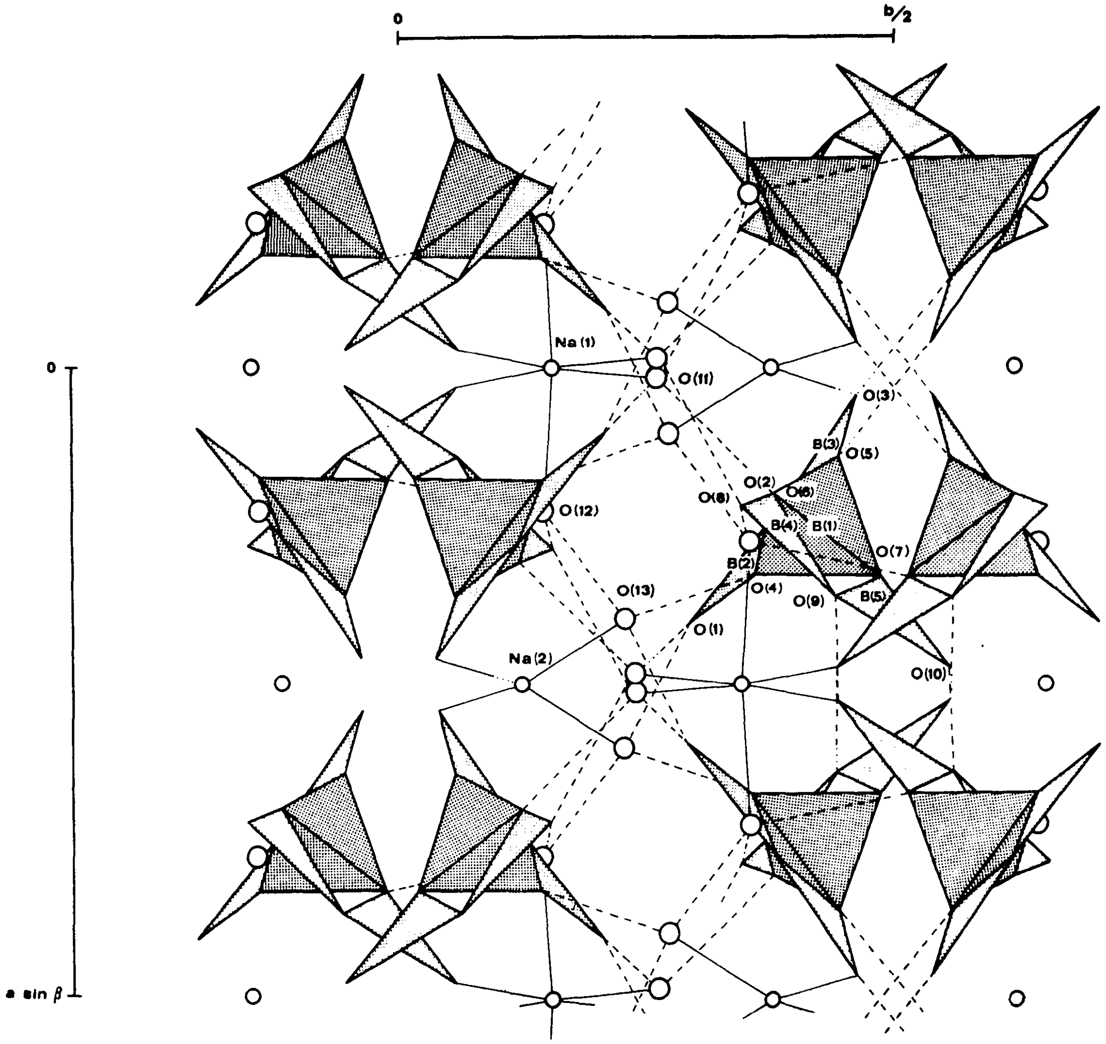


Fig. 1. The crystal structure of sborgite viewed along [001]. The continuous lines represent Na–O bonds; the dashed lines represent hydrogen bonds. Continuous and dashed lines ending with dots indicate that the bond is associated with an oxygen atom translated one unit in the [001] direction.

Symmetry code used in Tables 7, 8 and 9.

	x	y	z
None	x	y	z
i	$-\frac{1}{2}+x$	$-\frac{1}{2}+y$	z
ii	$1-x$	$1-y$	$1-z$
iii	$-x$	$1-y$	$-z$
iv	$\frac{1}{2}-x$	$\frac{1}{2}-y$	$1-z$
v	$\frac{1}{2}-x$	$\frac{1}{2}-y$	$-z$
vi	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$
vii	$1-x$	y	$\frac{1}{2}-z$
viii	$-x$	y	$\frac{1}{2}-z$
ix	$\frac{1}{2}-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$

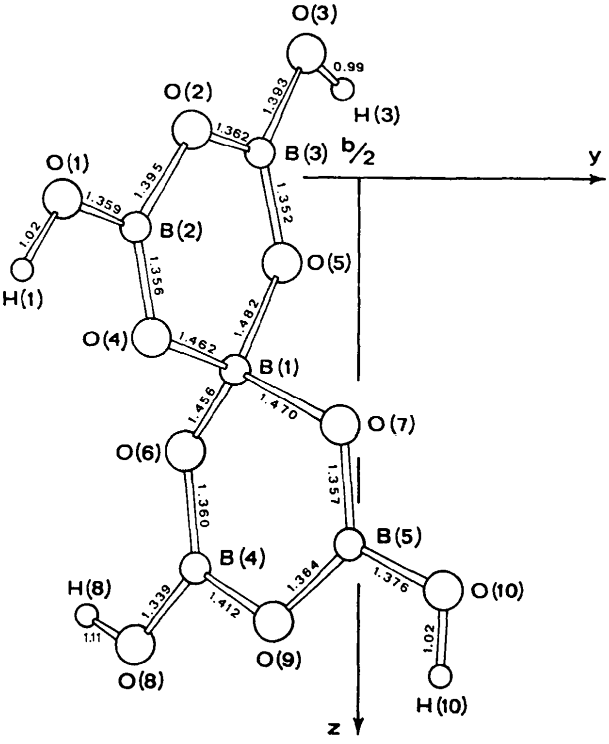


Fig. 2. Bond lengths in the pentaborate group. The group is viewed along [100].

Sodium coordination

The two sodium ions in the asymmetric unit are in special positions on a binary axis. Na–O bond lengths are given in Table 8. Na(1) is octahedrally coordinated by two O(10) hydroxyl ions and by four water molecules with a mean Na-O distance of 2·401 Å. The value is in very good agreement with the value 2·398 Å for ^{VI}Na–^{IV}O obtained on the basis of the effective ionic radii given by Shannon & Prewitt (1969). The Na(2) ion is coordinated tetrahedrally by two O(3) hydroxyl ions and two O(13) water molecules, with two other O(2) oxygen ions at a much larger distance (2·998 Å) corresponding to a valence bond strength of 0·03, calculated by the method of Donnay & Allmann (1970): we can thus assume that Na(2) has a coordination number four with two hydroxyl ions and two water molecules at the corners of an elongated tetrahedron (Fig. 1). Sodium with coordination number four has been found so far only in the crystal structures of Na_2O (Wyckoff, 1963), $Na_5P_3O_{10}$ (Corbridge, 1960) and $NaOH.H_2O$ (Wunderlich, 1957). Na_2O has the anti-fluorite structure: sodium is in tetrahedral coordination, but the Na–O distances are not known. The sodium coordination in sodium triphosphate is very irregular, the Na–O distances ranging from 2·22 to 2·68 Å with a mean value of 2·37 Å. In the crystal structure of $NaOH.H_2O$ there are pairs of edge-sharing sodium tetrahedra with Na–O bond lengths of 2·30, 2·35, 2·39 and 2·41 Å; the last two distances correspond to the oxygen atoms shared by two sodium atoms. From these data Shannon & Prewitt (1969) derived for $^{IV}Na^+$ an effective ionic radius of 0·99 Å, but they considered this doubtful, probably in view of the high irregularity of coordination in the case of $Na_5P_3O_{10}$ and the low accuracy of the data in the case of $NaOH.H_2O$; in fact the value shows a strong deviation from the radii *vs.* coordination number plot.

Thus it seemed useful, in view of the substantially tetrahedral coordination of Na(2) and the good accuracy of the present determination, to calculate a value for the effective ionic radius of $^{IV}Na^{+1}$ from our data. Taking into account that O(3) and O(13) have coordination numbers three (radius 1·357 Å) and four

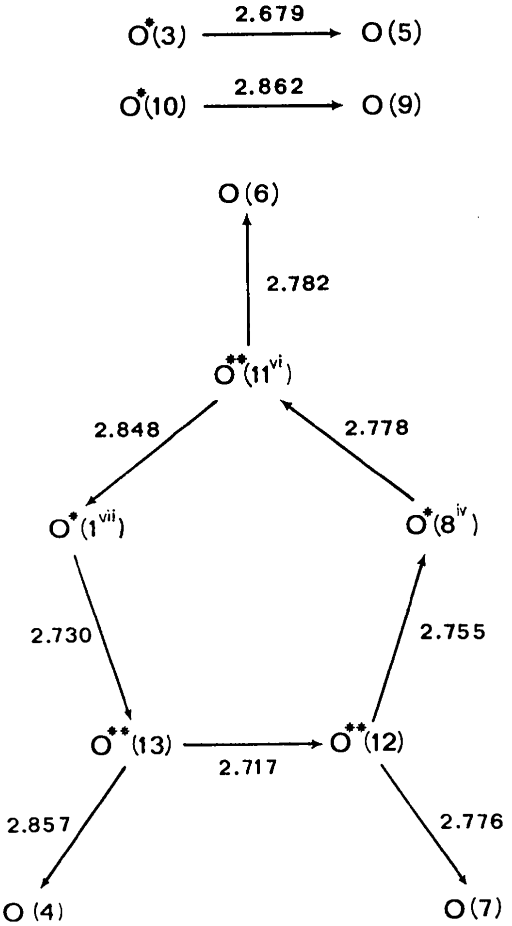
Table 7. *Mean-plane parameters and deviations of atoms from the plane*

The equation of the plane is in the form $Ax+By+Cz=D$, where x, y, and z are fractional coordinates, calculated after Schomaker, Waser, Marsh & Bergman (1959).

Plane	A	B	C	D	Atoms defining the plane
I	6·8903	12·8523	−2·1924	6·5145	O(1), O(2), O(3), O(4), O(5), B(2), B(3)
II	−8·3247	10·9099	3·5706	3·3785	O(6), O(7), O(8), O(9), O(10), B(4), B(5)
III	−5·8393	13·8760	1·2499	1·1576	$O(1^{vii})$, $O(8^{iv})$, $O(11^{vi})$, O(12), O(13)

Deviations from plane

I		II		III			
O(1)	−0·029 Å	O(6)	−0·005 Å	$O(1^{vii})$	−0·013 Å	$H(1^{vii})$	−0·007 Å
O(2)	0·050	O(7)	0·011	$O(8^{iv})$	−0·071	$H(8^{iv})$	0·067
O(3)	−0·035	O(8)	0·084	$O(11^{vi})$	0·053	$H(112^{vi})$	−0·038
O(4)	−0·003	O(9)	−0·145	O(12)	0·066	H(121)	−0·077
O(5)	−0·006	O(10)	0·072	O(13)	−0·036	H(132)	−0·325
B(2)	0·005	B(4)	−0·010				
B(3)	0·019	B(5)	−0·007				



	$\sum^{\rm I}_c v$	$\sum^{\rm II}_c v$
O*(1$^{\rm vii}$)	1·97	2·08
O*(8$^{\rm iv}$)	2·07	2·05
O**(11$^{\rm vi}$)	1·99	1·93
O**(12)	1·97	1·93
O**(13)	2·06	2·07
$\sum_j(\Delta v_j)^2$	0·010	0·024

Fig. 3. Hydrogen-bond system. The valence sums are given for each anion of the pentagonal ring. $\sum^{\rm I}_c v$ and $\sum^{\rm II}_c v$ correspond respectively to the left-handed and the right-handed system of arrows in the ring. $\Delta v_j=(\sum_c v)_j-2{\cdot}0$ is the deviation from the ideal value 2·0 of the valence sum of the jth oxygen atom.

(radius 1·378 Å) respectively, from the bond lengths Na(2)–O(3) 2·276 and Na(2)–O(13) 2·298 Å we calculate the values 0·919 and 0·920 Å respectively; thus the value 0·92 Å for the effective ionic radius of $^{\rm IV}$Na^{+1} can be assumed with good confidence.

Hydrogen bond system

From a list of all the distances shorter than 3·0 Å between oxygen atoms not bonded to the same cation, the system of hydrogen bonds given in Fig. 3 can be deduced. In this figure the oxygen atoms marked with one or two asterisks were indicated as hydroxyl ions and water molecules respectively by application of Christ's third rule.

An interesting feature of the hydrogen bond system in sborgite is the presence of pentagonal rings, which characterize the structures of the clathrate hydrates (Pauling, 1960). For the hydrogen bonds external to the pentagonal ring donor and acceptor oxygen atoms can be unambigously indicated. But for the hydrogen bonds of the pentagonal ring there is, beside the possibility indicated in the Figure (where the arrows go from the donor to the acceptor atoms), another possibility obtained by reversing the sense of the arrows in the ring. To test which of the two possibilities is correct we calculated the bond valence sums using the method of Donnay & Allmann (1970). In calculating hydrogen-bond valence strengths, use was made of the correlation between strength and length of hydrogen bonds given by Zachariasen (1963). The valence sum values for the five oxygen atoms of the ring strongly indicate that the first possibility (that represented in the Figure) for the hydrogen-bond system is the correct one. This was fully confirmed by a difference Fourier synthesis which showed well defined peaks in the predicted positions. Although in the present case the positions of the hydrogen atoms can be obtained from a difference synthesis, we think that in other less favourable cases the method of valence-sum calculations for testing the different possibilities of a hydrogen-bond system could be very useful.

The planarity of the pentagonal ring was tested by calculating the least-squares plane through the five

Table 8. *Bond lengths and angles in the sodium coordination polyhedra*

	Distance
Na(1)–O(11)	2·385 (4) Å
Na(1)–O(11$^{\rm viii}$)	2·385 (4)
Na(1)–O(12)	2·393 (4)
Na(1)–O(12$^{\rm viii}$)	2·393 (4)
Na(1)–O(10$^{\rm i}$)	2·425 (4)
Na(1)–O(10$^{\rm ix}$)	2·425 (4)
Na(2)–O(13)	2·298 (5) Å
Na(2)–O(13$^{\rm vii}$)	2·298 (5)
Na(2)–O(3$^{\rm v}$)	2·276 (4)
Na(2)–O(3$^{\rm vi}$)	2·276 (4)
Na(2)–O(2$^{\rm v}$)	2·998 (3)
Na(2)–O(2$^{\rm vi}$)	2·998 (3)

	Angle
O(11) –Na(1)–O(11$^{\rm viii}$)	83·5 (2)°
O(11) –Na(1)–O(12)	97·2 (1) [×2]
O(11) –Na(1)–O(12$^{\rm viii}$)	89·1 (1) [×2]
O(11) –Na(1)–O(10$^{\rm i}$)	172·7 (2) [×2]
O(11) –Na(1)–O(10$^{\rm ix}$)	89·3 (1) [×2]
O(12) –Na(1)–O(10$^{\rm i}$)	84·3 (1) [×2]
O(12) –Na(1)–O(12$^{\rm viii}$)	171·6 (2)
O(12) –Na(1)–O(10$^{\rm ix}$)	90·2 (1) [×2]
O(10$^{\rm i}$)–Na(1)–O(10$^{\rm ix}$)	97·9 (2)
O(13) –Na(2)–O(13$^{\rm vii}$)	83·3 (2)°
O(13) –Na(2)–O(3$^{\rm v}$)	139·2 (1) [×2]
O(13) –Na(2)–O(3$^{\rm vi}$)	100·2 (1) [×2]
O(3$^{\rm v}$)—Na(2)–O(3$^{\rm vi}$)	102·7 (2)

oxygen atoms. From the data of Table 7 it appears that the five hydrogen atoms involved in the five hydrogen bonds of the ring also lie approximately in the plane.

Bond lengths and angles involving hydrogen atoms were calculated assuming the coordinates obtained from the difference synthesis and are presented in Table 9. O–H bond lengths range from 0·93 to 1·11 Å with a mean value 1·03 Å.

Table 9. *Distances and angles involving hydrogen atoms*

Hydrogen bond	Distances			Angles
O–H···O	O–H	H···O	O···O	O–H··O
O(3)—H(3)·····O(5^{iii})	0·99 Å	1·74 Å	2·679 Å	157°
O(10)–H(10)····O(9^{ii})	1·02	2·05	2·862	135
O(1)—H(1)·····O(13^{vii})	1·02	1·72	2·730	178
O(13)–H(131)···O(4)	0·93	1·93	2·857	176
O(13)–H(132)···O(12)	1·02	1·79	2·717	149
O(12)–H(122)···O(7^{ix})	1·09	1·83	2·776	143
O(12)–H(121)···O(8^{iv})	1·02	1·75	2·755	169
O(8)—H(8)·····O(11^{viii})	1·11	1·67	2·778	172
O(11)–H(111)···O(6)	1·02	1·83	2·782	155
O(11)–H(112)···O(1^{v})	1·04	1·81	2·847	171

H–O–H angles	
H(111)–O(11)–H(112)	93°
H(121)–O(12)–H(122)	103
H(131)–O(13)–H(132)	116

Chidambaram, Sequeira & Sikka (1964) proposed a classification of hydrates based on the type of coordination of lone-pair orbitals of water. The lone-pair coordination of the three water molecules in sborgite is of the same type *G* in this classification scheme; that is, one of the lone pairs of electrons on each water molecule is directed approximately toward a monovalent metal ion, Na^+ in the present case, and the other lone pair is engaged in a hydrogen bond.

Crystal packing

The bond valence sums, calculated following the method of Donnay & Allmann (1970), are given in Table 10 for all the oxygen atoms; O* and O** represent respectively hydroxyl ions and water molecules. Satisfactory sums, ranging from 1·94 to 2·10, were found for each oxygen atom.

The building up of the crystal structure of sborgite, represented in Fig. 1, can be described as follows: the pentaborate group with atoms at x,y,z is linked through two hydrogen bonds of type O(3)···O(5) to the group with atoms at $-x,1-y,-z$, and through two other hydrogen bonds of the type O(9)···O(10) to the pentaborate group at $1-x,1-y,1-z$, thus giving a chain zigzagging along the [101] direction. An adjacent chain is generated by a *c*-glide plane; the connexion between the chains is effected by sodium coordination polyhedra. In fact Na(2) atoms on the one hand connect the two chains through two equivalent Na(2)–O(3) bonds and on the other hand are linked to two equivalent O(13) water molecules. In the same manner Na(1) atoms connect the chains through Na(1)–O(10) bonds and are linked to two equivalent O(11) water molecules. The pentaborate chains are thus connected in layers linked to each other through layers of O(11) and O(13) water molecules. A further connexion is made by the O(12) water molecule that is bonded to the Na(1) atom and makes three hydrogen bonds with the O(7) atom of one chain, the O(8) atom of the other chain, and the O(13) water molecule of the separating layer.

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References

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Chidambaram, R., Sequeira, A. & Sikka, S. K. (1964). *J. Chem. Phys.* **41**, 3616.

Christ, C. L. (1960). *Amer. Min.* **45**, 334.

Cipriani, C. (1957). *Rend. Accad. Nazl. Lincei*, **22**, 519.

Corbridge, D. E. C. (1960). *Acta Cryst.* **13**, 263.

Coulson, C. A. (1964). *Acta Cryst.* **17**, 1086.

Coulson, C. A. (1969). *Acta Cryst.* B**25**, 807.

Coulson, C. A. & Dingle, T. W. (1968). *Acta Cryst.* B**24**, 153.

Cruickshank, D. W. J. (1961). *J. Chem. Soc.* p. 5486.

Donnay, G. & Allmann, R. (1970). *Amer. Min.* **55**, 1003.

Table 10. *Bond valence sums in sborgite*

	B(1)	B(2)	B(3)	B(4)	B(5)	Na(1)	Na(2)	H	$\sum_c v$
O*(1)		1·02						0·95	1·97
O(2)		0·95	1·01						1·96
O*(3)			0·95				0·25	0·74	1·94
O(4)	0·76	1·03						0·18	1·97
O(5)	0·72		1·03					0·27	2·02
O(6)	0·77			1·02				0·21	2·00
O(7)	0·75				1·02			0·21	1·98
O*(8)				1·06				1·01	2·07
O(9)				0·92	1·00			0·18	2·10
O*(10)					0·98	0·16		0·82	1·96
O**(11)						0·17		1·82	1·99
O**(12)						0·17		1·80	1·97
O**(13)							0·25	1·81	2·06

International Tables for X-Ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
LEVY, H. A. (1956). *Acta Cryst.* **9**, 679.
LINGAFELTER, E. C. & DONOHUE, J. (1966). *Acta Cryst.* **20**, 321.
MERLINO, S. (1969). *Rend. Accad. Nazl. Lincei*, **47**, 85.
MERLINO, S. & SARTORI, F. (1969). *Acta Cryst.* **B25**, 2264.
MERLINO, S. & SARTORI, F. (1971). *Science*, **171**, 377.
PALM, J. M. (1964). *Acta Cryst.* **17**, 1326.
PANT, A. K. (1968). *Acta Cryst.* **B24**, 1077.
PAULING, L. (1960). *The Nature of the Chemical Bond.* 3rd Ed. Ithaca: Cornell Univ. Press.
SABELLI, C. (1962). *Mem. Soc. Tosc. Sci. Nat.* **69**, 299.
SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600.
SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* **B25**, 925.
STEWART, J. M. (1970). *X-ray System for Crystallographic Computing.* Computer Science Centre, Univ. of Maryland.
WUNDERLICH, J. A. (1957). *Acta Cryst.* **10**, 462.
WYCKOFF, R. W. G. (1963). *Crystal Structures*, **1**.
ZACHARIASEN, W. H. (1937). *Z. Kristallogr.* **98**, 266.
ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 385.
ZACHARIASEN, W. H. & PLETTINGER, H. A. (1963). *Acta Cryst.* **16**, 376.

Acta Cryst. (1972). **B28**, 3567

The Crystal Structure of Lidocaine Hydrochloride Monohydrate[*]

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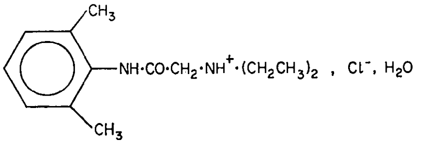
Crystals of the title compound, $C_{14}H_{22}N_2O.HCl.H_2O$, are monoclinic, $P2_1/c$, with $a=8{\cdot}490$ (5), $b=7{\cdot}110$ (5), $c=27{\cdot}58$ (2) Å, $\beta=106{\cdot}87$ (5)°, $Z=4$. 2385 of a possible 2694 independent reflexions in the range $\sin\theta/\lambda \le 0{\cdot}59$ were observed and measured diffractometrically. The crystal structure was determined by symbolic addition procedures and refined by block-diagonal least-squares calculations to a final R index of 0·11. There appears to be some disorder, with an alternative structure present at about 5% occupancy. Only the predominant structure has been characterized. This structure is fully hydrogen bonded, with adjacent lidocaine cations linked by water molecules into endless chains parallel to **b**. Adjacent chains related by the screw axes are joined in pairs by chloride ions. which bind N^+H and H_2O groups in different chains.

Introduction

The hydrogen-bonding properties of lidocaine in the hydrohexafluoroarsenate salt (I) have been studied by means of a determination of the crystal structure (Hanson, 1972). It also seemed of interest to study these properties in the hydrochloride monohydrate (II), as the environment of the lidocaine cation could be expected to approximate more closely the physiological environment in which it functions as a local anaesthetic. The hydrogen-bonding arrangement, and the conformation of the lidocaine cation, are found to be quite different in the two salts.



(II)

Experimental

Crystal data: F.W. 288·8, $V=1593$ Å^3, $D_m=1{\cdot}21$, $D_x=1{\cdot}20$ g.cm^{-3}, $\mu=21{\cdot}3$ cm^{-1} (Cu $K\alpha$). [The wavelength assumed for $\lambda(\alpha_1)$ was 1·54050 Å.] The space group was determined by the systematic absences evident on Weissenberg and precession photographs.

The material supplied (Astra Pharmaceuticals Ltd.) was recrystallized from a solution in ethyl acetate and acetone, yielding colourless translucent prisms. These were generally of high mosaicity, and many were twinned. The nominal dimensions of the specimen used were 0·42 × 0·31 × 0·45 mm. Cell dimensions and relative intensities were measured with a four-circle diffractometer and scintillation counter, using nickel-filtered Cu $K\alpha$ radiation with pulse-height discrimination. For the intensity measurements the specimen was mounted with **c** parallel to the φ axis; the θ–2θ scan mode was used (scans of 3° for $2\theta \le 50°$, 4° for $50° < 2\theta \le 100°$, 4·6° for $100° < 2\theta \le 130°$) with background counts measured at the beginning and end of each scan. Reflexions for which the net count was less than 7 (deca-) counts or less than 10% of the corresponding background count were considered to be unobserved. The intensities were corrected for absorp-

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