

The Crystal Structure of Pentapotassium Enneakaidekaborate, $5\text{K}_2\text{O} \cdot 19\text{B}_2\text{O}_3$

BY J. KROGH-MOE

Chemistry Department, University of Trondheim, Trondheim, Norway

(Received 30 January 1974; accepted 23 February 1974)

Potassium borate glasses of the tetraborate composition, $\text{K}_2\text{O} \cdot 4\text{B}_2\text{O}_3$, may be crystallized to give a compound of the composition $\text{K}_2\text{O} \cdot 3.8\text{B}_2\text{O}_3$ or $5\text{K}_2\text{O} \cdot 19\text{B}_2\text{O}_3$. This phase is monoclinic, space group $C2/c$, with unit-cell dimensions at 22°C : $a = 17.888 \pm 0.002$, $b = 11.479 \pm 0.001$, $c = 12.973 \pm 0.002 \text{ \AA}$, $\beta = 95.52 \pm 0.01^\circ$. The calculated density is 2.247 g cm^{-3} with two formula units of $5\text{K}_2\text{O} \cdot 19\text{B}_2\text{O}_3$ in the cell. The structure was determined by direct methods from three-dimensional X-ray data taken with Mo $K\alpha$ radiation. A full-matrix least-squares refinement resulted in an R value of 0.030 (0.026 for the weighted R value). The borate anion polymer in this structure forms a three-dimensional framework consisting of interconnected pentaborate groups, triborate groups, BO_4 tetrahedra and BO_3 triangles. Boron–oxygen bond lengths (standard deviation 0.002 \AA) are normal and with the usual differences depending on the location within the groups. The structure has three crystallographically different potassium atoms. The closest potassium–oxygen approach is 2.681 \AA .

Introduction

A phase diagram of the system potassium oxide–boron was reported by Rollet (1935). The correctness of this phase diagram in the tetraborate ($\text{K}_2\text{O} \cdot 4\text{B}_2\text{O}_3$) region was questioned by Krogh-Moe (1961), who was unable to prepare a crystalline phase which he could unequivocally identify as a tetraborate. A monoclinic phase, with C -centring, was erroneously conjectured by Krogh-Moe (1961) to be $\gamma\text{-K}_2\text{O} \cdot 5\text{B}_2\text{O}_3$. One of the reasons for this assignment was the densities calculated from the unit-cell dimensions. A pentaborate with 8 formula units of $\text{K}_2\text{O} \cdot 5\text{B}_2\text{O}_3$ in the cell would correspond to a density of 2.216 g cm^{-3} for this phase, whereas a tetraborate with 8 formula units of $\text{K}_2\text{O} \cdot 4\text{B}_2\text{O}_3$ would only give 1.867 g cm^{-3} . The former density is close to the expected value, whereas the latter was considered too low. If a simple stoichiometry is assumed these remain the only two possibilities, since a tetraborate with 9 or 10 formula units in the cell requires positions of low multiplicity which are unavailable in the space group. As the present work has revealed, however, this phase actually has a composition $\text{K}_2\text{O} \cdot 3.8\text{B}_2\text{O}_3$ with 10 formula units in the cell, giving a calculated density of 2.247 g cm^{-3} . The phase is therefore neither a pentaborate, nor a tetraborate, though it is closer in composition to the latter. Thus the presence of a tetraborate in the phase diagram for the system potassium oxide–boron oxide has not yet been confirmed.

The monoclinic C -centred potassium borate phase is the subject of the present crystal structure study. The rather unusual stoichiometry adds interest to a complete structure study of this phase.

Experimental

Crystalline $5\text{K}_2\text{O} \cdot 19\text{B}_2\text{O}_3$ was prepared by fusing in a platinum crucible potassium diborate tetrahydrate

($\text{K}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$, Riedel de Haen, A.G.) with boric acid (H_3BO_3 , Merck, p.a.) in a stoichiometric ratio corresponding to the tetraborate composition. The $\text{K}_2\text{O} \cdot 4\text{B}_2\text{O}_3$ glass obtained, was crystallized at temperatures around 750°C .

A single crystal, approximately prismatic in shape with dimensions $0.013 \times 0.022 \times 0.036 \text{ cm}$, was used. Intensity data were obtained with an on-line Picker single crystal automatic diffractometer and Mo $K\alpha$ radiation. Measurements were made at 3325 different reciprocal lattice points, subject to the condition $h+k=2n$. 3078 reflexions not affected by systematic extinctions were observed larger than the background.

Unit-cell dimensions and standard deviations, $a = 17.888 \pm 0.002$, $b = 11.479 \pm 0.001$, $c = 12.973 \pm 0.002 \text{ \AA}$, $\beta = 95.52 \pm 0.02^\circ$, were obtained by the method of least-squares from angle data recorded at 22°C for 12 high-angle reflexions (based on the wavelength 0.7093 \AA for Mo $K\alpha_1$). With 2 formula units of $5\text{K}_2\text{O} \cdot 19\text{B}_2\text{O}_3$ in the cell, the calculated density is 2.247 g cm^{-3} .

Structure determination

The observed intensities were converted to structure factors in the usual manner. A correction for absorption was also made, but since the linear absorption coefficient ($\sim 9 \text{ cm}^{-1}$) is small, the maximum correction amounted to only 1.5 per cent in the structure factors.

The observed systematic extinctions are those required by the space group $C2/c$. A statistical test of the distribution of normalized structure factors gave a strong indication of a centre of symmetry in agreement with the space group assignment. The structure was determined by direct methods, using the program system developed by Germain, Main & Woolfson (1971). The set of signs with the highest ‘figure of merit’ proved to give a sensible structure. The structure was refined by the method of least-squares, using the full-matrix *LSFIV01* program by Borgen & Mestvedt

(1973). All the 3078 reflexions observed above the background were included in the refinement. The atomic scattering factors for B, O and K⁺, used for calculating the structure factors, were taken from *Internat-*

tional Tables for X-ray Crystallography (1962). The refinement was carried out with a weighting scheme based on the statistical counting errors compounded with errors assumed to be 1% of the observed in-

Table 1. Final observed and calculated structure factors.

The columns are 1, $10F_o$ and $10F_c$. Reflexions affected by extinction are marked with an asterisk.

23+L		-16+L		9 210 210 5 565		3 111 111 5 565		9 308 310 6 600		2 65 257 -8-6L		-5-6L		-4-10L		
3 105 109	309	321	6 462 633	3 257 263	1 195 135	7 270 270	-10+L	13 372 371	6 60	93	16 167 156	12 115 127	9 453 461	6 123 111	7 137 129	
3 97 102	307	272	6 462 633	2 192 176	0 239 238	6 1036 1037	7 1 61	63	11 43 406	-7-9L	12 513 501	10 314 308	9 288 304	6 115 104	5 256 250	
0 88 63	374	474	2 87 76	50 385	0 -12+12L	5 501 501	12 826 826	10 161 168	10 207 197	5 264 255	3 305 314	3 262 245	3 262 245	3 262 245	3 262 245	
-22+L	L	2 87 76	3 575 573	0 -16+6L	5 416 422	3 65 45	10 156 156	12 133 132	12 503 506	9 207 197	8 629 651	6 322 322	0 150 150	1 295 295	0 238 229	
3 207 233	373	373	57 31	1 205 205	0 316 314	4 651 651	8 79 86	10 337 343	4 451 451	5 659 705	2 311 299	-3-7L	3 170 173	-2-7L	-2-7L	
6 66 71	-18+6L	10 155 155	5 565 558	-11+7L	3 241 250	7 463 463	9 493 505	9 129 110	3 170 173	2 725 728	18 222 223	16 255 256	16 255 256	16 255 256	16 255 256	
1 633 419	9 252 255	0 353 364	11 171 170	2 253 253	0 30 30	5 241 250	1 860 860	5 575 570	16 274 274	261	0 347 349	11 121 91	19 850 866	19 76 67	19 76 67	
-22+2L	L	1 63 149	12 106 63	6 73 63	80 -12+12L	12 366 371	16 370 371	12 124 121	4 929 929	15 181 170	10 347 349	-4+6L	10 347 349	9 85 85	12 763 759	
6 732 742	5 237 410	10 110 110	5 482 482	0 276 276	10 129 129	15 103 103	3 111 111	3 617 617	13 1119 1107	15 99 99	9 96 96	11 646 646	11 646 646	8 845 845	8 845 845	
5 230 234	6 242 255	8 262 255	3 607 595	5 168 170	6 554 557	13 573 573	4 856 856	1 324 324	0 328 327	15 656 629	15 99 99	9 96 96	11 646 646	11 646 646	8 845 845	
3 50 50	216 201	3 200 199	3 348 361	6 185 195	6 99 100	11 110 110	6 810 810	12 234 219	15 187 169	10 493 493	11 197 197	5 271 350	6 1245 1245	6 1245 1245	5 1245 1245	
2 439 445	5 568 569	5 170 170	0 949 949	5 603 602	5 360 367	10 805 810	12 288 298	9 356 356	10 250 250	9 942 863	11 197 197	5 271 350	6 1245 1245	6 1245 1245	5 1245 1245	
1 202 233	2 223 235	0 105 105	6 161 633	3 215 222	8 239 241	9 151 151	6 167 167	10 497 494	9 250 250	7 570 570	5 942 947	3 288 303	6 1245 1245	6 1245 1245	5 1245 1245	
-22+6L	L	2 62 62	8 537 537	-16+4L	3 99 99	4 489 487	9 151 151	9 509 509	9 225 225	10 250 250	7 570 570	5 942 947	3 288 303	6 1245 1245	6 1245 1245	5 1245 1245
6 107 85	5 583 576	10 220 202	12 107 119	0 173 180	0 466 466	5 340 340	5 389 379	7 190 190	7 265 267	9 982 982	6 246 246	0 239 239	0 126 113	1 1192 1210	0 57 19	
4 242 242	5 253 256	10 261 261	12 107 119	0 173 180	0 466 466	5 340 340	5 389 379	7 190 190	7 265 267	9 982 982	6 246 246	0 239 239	0 126 113	1 1192 1210	0 57 19	
-21+1L	L	6 116 405	10 200 291	8 308 308	12 367 367	11 365 367	10 162 162	10 1652 1651	3 374 376	3 466 466	6 252 252	0 309 318	15 13 13	4 491 490	16 420 488	-2+6L
6 459 459	3 456 438	10 440 425	5 852 853	9 380 380	8 469 478	9 151 151	9 355 355	1 543 539	0 620 620	5 166 166	0 269 269	11 182 189	14 718 703	14 718 703	14 718 703	
6 200 273	1 630 630	9 231 231	3 516 516	2 627 627	5 216 214	11 150 150	15 233 226	5 256 256	13 206 206	15 90 90	13 183 185	5 222 223	2 241 241	6 186 208	9 982 988	
3 472 460	-16+2L	4 769 769	0 696 707	6 216 216	3 340 340	12 164 164	15 233 226	5 256 256	13 206 206	15 90 90	13 183 185	5 222 223	2 241 241	6 186 208	9 982 988	
3 302 302	3 415 415	6 105 105	1 307 307	12 160 160	12 160 160	11 150 150	15 233 226	5 256 256	13 206 206	15 90 90	13 183 185	5 222 223	2 241 241	6 186 208	9 982 988	
0 576 576	10 705 724	7 75 75	1 307 307	0 334 332	0 334 332	-11+11L	6 161 423	7 671 675	16 960 960	4 483 483	11 182 189	14 718 703	14 718 703	14 718 703	14 718 703	
-21+3L	L	7 567 579	-16+0L	1 208 208	0 334 332	0 334 332	-12+6L	8 251 266	8 251 266	8 251 266	8 251 266	8 251 266	8 251 266	8 251 266	8 251 266	-3+11L
7 167 156	5 502 497	12 184 184	16 184 184	11 321 321	12 367 367	13 76 25	6 297 283	13 140 140	15 102 102	15 159 159	11 1076 1083	15 73 73	2 606 599	27 395 395	27 395 395	
5 207 219	7 601 607	8 1021 1019	8 337 337	12 256 256	6 297 283	13 140 140	15 102 102	15 159 159	11 1076 1083	15 73 73	2 606 599	27 395 395	27 395 395	27 395 395		
4 68 93	5 331 329	7 126 126	11 321 321	12 367 367	13 76 25	6 297 283	13 140 140	15 102 102	15 159 159	11 1076 1083	15 73 73	2 606 599	27 395 395	27 395 395		
1 196 202	1 801 801	5 1156 1156	5 1185 1185	9 454 454	5 257 257	9 360 360	10 178 178	12 226 221	11 216 216	11 216 216	12 226 221	11 216 216	12 226 221	11 216 216	-1+1L	
0 230 237	5 591 592	11 344 344	5 375 355	6 267 267	2 605 605	10 186 186	9 365 365	8 388 388	1 451 451	9 365 365	8 388 388	0 397 397	1 451 451	9 365 365	-1+1L	
-21+5L	L	2 255 255	6 366 366	0 151 151	-10+1L	6 151 151	-11+11L	6 151 151	6 151 151	-5+5L	-6+2L	15 327 316	14 373 373	14 373 373	-4+4L	-4+4L
5 560 542	10 194 178	13 270 268	13 270 268	13 270 268	13 270 268	13 270 268	13 270 268	13 270 268	-6+6L	15 327 316	14 373 373	14 373 373	14 373 373	14 373 373	-3+11L	
4 99 77	6 47 63	11 303 363	10 363 363	3 266 304	12 256 256	6 297 283	13 140 140	15 102 102	15 159 159	11 1076 1083	15 73 73	2 606 599	27 395 395	27 395 395	27 395 395	
3 605 605	10 99 103	10 780 780	-10+6L	12 256 256	6 297 283	13 140 140	15 102 102	15 159 159	11 1076 1083	15 73 73	2 606 599	27 395 395	27 395 395	27 395 395		
2 245 245	1 161 161	1 161 161	1 161 161	1 161 161	1 161 161	1 161 161	1 161 161	1 161 161	-10+10L	15 327 316	14 373 373	14 373 373	14 373 373	14 373 373	-3+11L	
0 179 180	6 605 605	1 161 161	-15+5L	2 255 255	6 297 283	13 140 140	15 102 102	15 159 159	11 1076 1083	15 73 73	2 606 599	27 395 395	27 395 395	27 395 395	27 395 395	
-20+1L	L	5 677 678	5 677 678	5 677 678	5 677 678	5 677 678	-12+12L	5 677 678	-10+12L	5 677 678	-9+7L	8 571 583	1 350 349	0 1013 988	-2+19L	-2+19L
8 255 251	12 329 332	4 116 116	11 324 324	12 256 256	6 297 283	13 140 140	15 102 102	15 159 159	11 1076 1083	15 73 73	2 606 599	27 395 395	27 395 395	27 395 395	27 395 395	
5 104 104	3 336 336	5 256 256	10 405 405	10 405 405	10 405 405	10 405 405	10 405 405	10 405 405	-10+10L	8 571 583	1 350 349	0 1013 988	-2+19L	-2+19L		
5 614 616	7 202 207	4 207 207	5 595 595	5 132 132	5 236 236	5 236 236	12 225 225	12 225 225	12 225 225	12 225 225	12 225 225	12 225 225	12 225 225	12 225 225	-1+5L	
2 459 467	10 57 57	4 677 669	6 634 620	1 161 161	2 666 685	6 639 641	4 124 124	2 666 685	2 666 685	1 451 451	2 666 685	1 451 451	1 451 451	1 451 451	-1+5L	
1 153 153	7 174 174	1 174 174	1 174 174	1 174 174	1 174 174	1 174 174	1 174 174	1 174 174	-10+10L	8 571 583	1 350 349	0 1013 988	-2+19L	-2+19L		
0 842 836	7 400 308	1 202 253	1 202 253	1 202 253	1 202 253	1 202 253	1 202 253	1 202 253	-13+5L	8 571 583	1 350 349	0 1013 988	-2+19L	-2+19L		
9 6 60	3 905 913	12 91 91	12 91 91	12 91 91	12 91 91	12 91 91	12 91 91	12 91 91	-15+5L	8 571 583	1 350 349	0 1013 988	-2+19L	-2+19L		
7 245 242	1 166 166	1 166 166	1 166 166	1 166 166	1 166 166	1 166 166	1 166 166	1 166 166	-10+10L	8 571 583	1 350 349	0 1013 988	-2+19L	-2+19L		
5 671 678	0 865 865	117 670	659 659	275 275	7 372 370	9 323 317	12 161 161	7 716 716	13 502 501	12 203 202	1 376 376	3 304 304	0 255 255	0 255 255	0 255 255	
4 601 605	1 167 167	1 167 167	1 167 167	1 167 167	1 167 167	1 167 167	1 167 167	1 167 167	-10+10L	8 571 583	1 350 349	0 1013 988	-2+19L	-2+19L		
2 272 266	1 181 181	1 181 181	1 181 181	1 181 181	1 181 181	1 181 181	1 181 181	1 181 181	-10+10L	8 571 583	1 350 349	0 1013 988	-2+19L	-2+19L		
1 630 630	11 310 301	7 345 345	5 116 116	3 265 265	6 363 354	5 103 103	16 207 207	4 376 376	12 160 159	1 376 376	3 304 304	0 255 255	0 255 255	0 255 255	0 255 255	
0 601 600	10 283 283	4 262 257	2 257 257	2 257 257	2 257 257	2 257 257	2 257 257	2 257 257	-10+10L	8 571 583	1 350 349	0 1013 988	-2+19L	-2+19L		
0 245 242	2 244 244	3 261 261	1 261 261	1 261 261	1 261 261	1 261 261	1 261 261	1 261 261	-10+10L	8 571 583	1 350 349	0 1013 988	-2+19L	-2+19L		
8 665 670	6 671 685	2 459 467	0 459 30	3 267 267	8 666 666	4 185 200	5 64 56	7 453 476	12 428 415	1 376 376	3 304 304	0 255 255	0 255 255	0 255 255	0 255 255	
6 179 186	0 245 254	1 167 167	1 167 167	1 167 167	1 167 167	1 167 167	1 167 167	1 167 167	-10+10L	8 571 583	1 350 349	0 1013 988	-2+19L	-2+19L		
2 462 466	3 415 412	10 75 75	10 75 75	10 75 75	10 75 75	10 75 75	10 75 75	10 75 75	-13+7L	8 571 583	1 350 349	0 1013 988	-2+19L	-2+19L		
0 345 345	5 603 603	1 167 167	1 167 167	1 167 167	1 167 167	1 167 167	1 167 167	1 167 167	-10+10L	8 571 583	1 350 349	0 1013 988	-2+19L	-2+19L		
1 526 530	-16+10L	3 261 259	15 61 61	15 61 61	15 61 61	15 61 61										

Table 1 (*cont.*)

3-13-L	3 972	972	2 19	131	3.9-L	4,0-L	5 285	379	7 569	568	9-L	8 62	639	0 56	60	8 738	737	2 881	854	18-L-L
3 21	273	1 1077	1062	0 99	105	2 6-L	12 273	261	16 295	292	3 61	59	559	568	16 360	355	2 250	264	12-L-L	
5 48	508	340	330	0 77	65	2 6-L	12 209	301	12 477	477	5 51	59	591	591	12 1201	1201	2 265	1 775	773	
3 99	64	1-3-L	15 180	180	9 109	25	10 267	297	0 411	416	1 571	571	11 49	49	3 500	564	3 330	331	1 45	
1 303	32	16	93	59	13 234	214	7 545	566	6 204	181	6 6-L	6 6-L	10 718	711	10 4-L-L	7 50	150	123	0 123	
0 501	496	15	369	365	12 785	760	6 68	92	4 883	904	1 231	111	12 229	223	11 250	239	8 670	604	4 356	
0 14-L	13	43	102	10	235	224	4 195	198	0 190	126	12 229	223	11 250	239	8 670	604	4 356	357	1 151	
3 42-L	813	113	113	0 77	65	2 6-L	12 209	301	12 477	477	9 271	264	5 114	114	9 6	637	643	0 182	180	
4 102	97	49	106	9 109	7	1309	1303	1 196	199	9 271	264	5 114	114	9 6	637	643	0 182	180		
3 14-L	143	9	1209	1195	6 1140	1120	0 111	97	15 183	133	8 145	133	7 323	295	2 64	53	7 320	321	12-L-L	
1 49	49	70	60	6 3	319	301	3-L-L	13 139	117	6 481	481	10 303	306	1 1750	1530	7 149	1485	1 211		
0 36-L	300	1	126	1238	3 305	516	12 677	678	5 57	117	4 262	193	9 345	345	9-L	5 58	20	9 26	356	
0 112-L	1	136	1208	1 263	231	10 138	156	3 251	105	1 198	106	3 173	173	3 277	277	5 217	202	5 173		
9 157	19-L	1	370	403	2 220	222	8 127	161	9 259	251	2 629	621	1 158	158	13 461	457	1 119	119	4 408	
5 450	500	1	612	262	290	2-L-L	6 416	394	7 1161	1133	0 140	195	12 321	327	0 57	58	352	337	2 165	
3 336	426	436	15	480	668	5 567	6 638	632	7 711	11-L	10 273	282	10 2-L-L	5 394	407	0 163	142	3 625	624	0 594
5 223	221	1	154	269	266	7 712	719	4 1350	1345	6 6-L	6-L	9 217	217	1 301	293	2 250	255	1 19-L-L		
3 99	109	15	732	703	2 207	307	5 231	255	3 1208	1304	13 619	633	8 504	507	9 801	802	13 124	110	0 325	
5 350	450	428	119	209	1 207	307	5 450	447	1 73	59	12 81	72	170	183	5 500	512	11 414	416	12-L-L	
0 126	118	118	118	118	118	5 550	557	3-L-L	9 233	267	3 63	117	2 625	623	9 198	198	11 216	186	0 162	
11 118	1155	8	550	557	5 550	557	5-L-L	9 233	267	3 63	117	2 625	623	9 198	198	11 216	186	0 162		
0 10-L	9	317	303	6	204	281	26	12 186	187	15 183	187	9 662	696	2 111	101	1 1289	1285	7 647		
12 243	232	232	16	168	168	5 168	5 168	12 167	165	4 116	140	12 167	165	0 169	169	11 169	169	6 600		
10 36-L	385	12	216	195	2 200	192	5 249	256	10 416	426	7 207	209	7 153	155	10 834	829	6 208	208	1 177	
9 120	122	216	195	1 173	85	1 266	281	9 167	168	1 389	394	1 205	204	2 148	140	9 215	204	1 711		
9 616	609	3	163	163	0 240	209	2 217	225	8 177	177	7 168	168	0 169	169	6 600	595	1 167	167	0 169	
20 210	210	152	147	147	147	147	147	147	7 168	162	5 161	155	10 203	204	2 141	141	5 167	167	0 169	
9 537	540	1	1147	1079	2-L-L	6 315	303	6-L-L	7 168	162	5 161	155	10 203	204	10 0-L-L	6 528	534	1 238	227	
3 231	226	1	16	686	680	8 271	267	10 195	195	5 209	209	0 402	505	9 256	256	12 165	165	4 407		
1 637	636	1	17-L	16	168	168	5 168	168	12 167	165	4 116	140	12 167	165	0 169	169	10 27	293	0 193	
0 415	425	15	333	348	12 680	680	1 361	362	9 168	163	12 238	238	0 347	348	8 602	611	10 612	603	7 711	
0 6-L	22	35	10	109	93	93	93	93	9 155	155	10 600	591	9 347	348	8 602	611	10 612	603	7 711	
11 293	288	9	191	181	3-L-L	9 570	570	5-L-L	9 570	570	5 160	160	12 237	237	9 575	565	1 19-L-L	9 575	565	
13 114	131	9	202	209	7	1315	9 125	9 125	15 246	260	7 347	348	5 160	160	12 237	237	11 166	167	0 173	
5 513	509	8	125	126	6 637	637	3 363	360	10 484	482	12 1265	1270	2 231	237	9 571	567	1 19-L-L	9 571	567	
13 393	403	5	787	787	4 173	173	9 166	166	12 237	237	3 363	360	10 484	482	12 1265	1270	2 231	237	9 571	
9 350	345	4	82	82	8 165	165	5 359	325	10 261	269	3 363	360	10 484	482	12 1265	1270	2 231	237	9 571	
7 346	352	2	160	160	1 199	199	5 221	221	10 249	249	8 165	165	5 359	325	10 261	269	1 19-L-L	9 571	567	
6 447	455	1	369	381	0 17	2	167	161	7 165	156	1 542	562	10 166	165	8 105	105	1 167	167	0 169	
4 504	498	1	113	109	2-L-L	6 511	518	5-L-L	9 515	518	5 160	160	12 167	165	8 105	105	1 167	167	0 169	
3 184	174	1	19-L	16	162	162	8 822	820	4-L-L	6 518	518	5 160	160	12 167	165	8 105	105	1 167		
1 600	480	15	73	72	8 122	120	2 236	234	10 195	195	7 165	165	8 105	105	1 167	167	0 169			
0 1155	151	1	234	224	10 1203	1196	11 315	321	1 503	508	12 167	165	8 105	105	1 167	167	0 169			
0 6-L	34	34	30	16	159	159	9 109	96	10 164	163	1 503	508	12 167	165	8 105	105	1 167	167	0 169	
15 410	410	7	768	821	4 2361	2573	8 126	106	5 57-L	57-L	8 167	870	1 277	270	11 3-L-L	9 371	371	1 19-L-L	9 371	
17 71	6	255	250	0 241	241	6 86	83	13 127	131	8 167	161	1 542	562	10 166	165	8 105	105	1 167		
13 65	65	5	895	912	5 168	168	5 168	168	12 167	165	8 167	161	1 542	562	10 166	165	8 105	105	1 167	
11 164	167	3	211	218	5 168	168	3-L-L	9 303	303	11 213	223	5 168	168	12 167	165	8 105	105	1 167		
10 478	478	1	235	235	16 363	370	2 54	53	10 445	459	7 166	165	12 167	165	8 105	105	1 167	167	0 169	
9 105	102	0	904	904	14 367	370	3 54	53	9 329	329	7 168	162	1 542	562	10 166	165	8 105	105	1 167	
7 157	180	1	111	111	11 480	476	5 366	363	9 345	343	7 168	162	1 542	562	10 166	165	8 105	105	1 167	
6 160	160	1	112	112	5 168	168	5 168	168	12 167	165	8 167	161	1 542	562	10 166	165	8 105	105	1 167	
5 16-L	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16-L-L	
12 219	219	16	168	167	7 163	162	9 105	107	4 156	155	12 167	165	8 167	161	1 542	562	10 166	165	8 105	
7 294	294	8	165	165	237	237	237	237	7 163	162	9 105	107	4 156	155	12 167	165	8 167	161	1 542	
8 143	101	5	327	327	16 371	363	11 402	412	8 165	163	2 246	247	3 308	315	10 323	323	8 167	165	1 542	
7 109	71	2	414	416	9 165	165	9 165	165	12 167	165	8 167	161	2 246	247	3 308	315	10 323	323	8 167	
3 2265	2380	0	97	95	8 167	165	8 167	165	12 167	165	8 167	161	2 246	247	3 308	315	10 323	323	8 167	
1 20	20	5	210-L	210-L	6 1635	1635	6 87	86	12 167	165	8 167	161	2 246	247	3 308	315	10 323	323	8 167	
0 1110	1131	0	546	546	11 511	511	6 167	165	9 165	163	1 246	247	3 308	315	10 323	323	8 167	165	1 542	
11-L	1-L	1-L	1-L	1-L	1-L	1-L	1-L	1-L	1-L	1-L	1-L	1-L	1-L	1-L	1-L	1-L	1-L	1-L	1-L-L	
27	27	2-L-L	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16-L-L	
70	70	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15-L-L	
62	619	15	163	163	6 637	636	6 836	823	4-L-L	167	167	167	167	167	167	167	167	167	167-L-L	
52	52	16	163	163	6 637	636	6 836	823	4-L-L	167	167	167	167	167	167	167	167	167	167-L-L	
465	470	7	72	72	3 470	474	5 154	152	12 167	165	8 167	161	1 246	247	3 308	315	10 323	323	8 167	
289	285	6	163	163	234	234	11 256	275	7 7-L	7-L	12 167	165	8 167	161	1 246	247	3 308	315	10 323	
304	304	5	246	246	11 205	205	8 167	165	12 167	165	8 167	161	1 246	247	3 308					

tensity. The structure initially refined to an R value of 0.031 (and 0.028 for the weighted R value). The 15 reflexions with the strongest intensities were systematically calculated larger than observed. They were therefore assumed to be affected by extinction and were removed from the data set. The structure now finally

refined to an R value of 0.030 or 0.026 for the weighted R value. During the last cycle of refinement the largest shift to error ratio was 0.15. The observed and calculated structure factors are given in Table 1. The final atomic coordinates and the thermal parameters are given in Table 2.

Discussion of the structure

Fig. 1 shows a section of the three-dimensional borate framework in pentapotassium enneakaidekaborate,

$5\text{K}_2\text{O} \cdot 19\text{B}_2\text{O}_3$, as a stereo-pair projected approximately along the b axis. (The seemingly cluttered stereo-pair becomes well resolved, when viewed in a stereoscope.) The framework consists of pentaborate and triborate

Table 2. Final atomic parameters

Positional parameters are expressed as a fraction of the cell edge, and temperature factors are of the form $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. All values are multiplied by 10^5 . Atoms K(3), O(10) and B(9) occupy special positions.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K(1)	16416	45610	19611	99	809	252	57	60	161
K(2)	32477	26876	33243	91	307	203	8	26	14
K(3)	0	0	0	257	506	348	-203	-142	193
O(1)	38887	49123	33223	78	304	186	22	25	64
O(2)	8684	11377	30914	91	364	276	-54	77	-141
O(3)	20182	13754	23162	83	302	187	-37	45	-74
O(4)	14949	13634	5444	155	404	167	151	63	76
O(5)	26955	45204	5709	125	407	164	125	51	93
O(6)	26297	48578	38048	83	251	127	-41	22	-19
O(7)	8667	42095	36406	74	292	187	25	47	94
O(8)	2328	38306	5034	71	233	198	-16	43	-65
O(9)	8612	26616	49202	66	183	180	-4	27	37
O(10)	0	96934	25000	70	204	291	0	27	0
O(11)	31465	9811	49803	83	249	145	-47	20	-16
O(12)	17457	26533	36157	79	246	230	-15	46	-76
O(13)	35774	31658	12547	100	422	182	111	55	112
O(14)	47740	27373	6899	91	163	168	11	40	-10
O(15)	43329	18112	21765	70	228	159	36	20	39
O(16)	47649	3853	33476	68	200	146	4	12	38
B(1)	17640	6401	14337	85	248	144	19	26	-7
B(2)	6760	2481	24090	71	217	183	23	-3	27
B(3)	15439	17271	30182	82	230	166	5	13	4
B(4)	32680	37602	3951	73	265	202	20	21	45
B(5)	23818	47702	47603	61	218	155	7	15	-14
B(6)	13208	33756	42846	64	199	153	-13	28	0
B(7)	1455	29478	50453	80	178	123	-20	13	-36
B(8)	1568	44983	38214	84	194	118	-18	1	-13
B(9)	0	60911	25000	66	171	137	0	9	0
B(10)	42428	25268	13623	83	184	148	10	16	-35
Standard deviations									
K	2	4	3	1	4	3	2	1	3
O	5	9	8	3	8	6	4	4	6
B	9	15	13	5	13	9	6	5	9

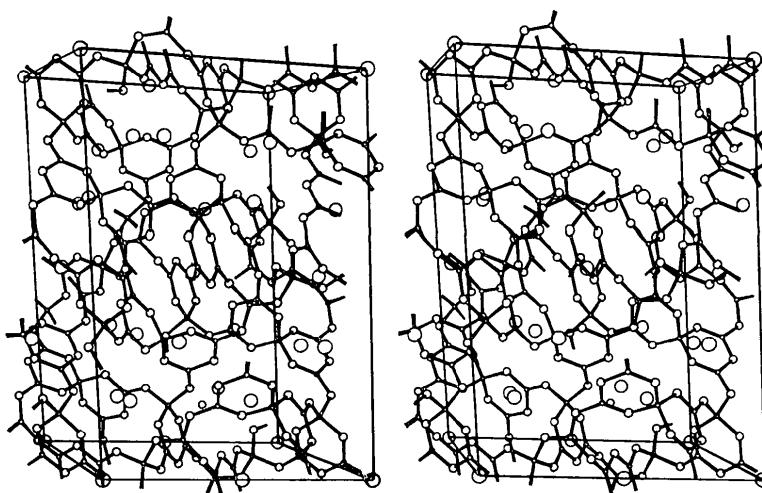


Fig. 1. Stereopair showing the boron–oxygen framework and the potassium atom positions in $5\text{K}_2\text{O} \cdot 19\text{B}_2\text{O}_3$. The large open circles, not connected by lines, represent the potassium atoms. Unit-cell edges are also shown. The b axis is approximately perpendicular to the paper plane; the c axis and the a axis are approximately horizontal and vertical respectively.

groups in equal amounts as well as BO_4 tetrahedra and BO_3 triangles which are not part of any larger groups.

Our 5:19 borate may be taken as a pseudotetraborate with an oxide ratio 1:3.8. The compound is actually found to be structurally related to some 1:4 tetraborates previously studied. Thus $\text{Ag}_2\text{O} \cdot 4\text{B}_2\text{O}_3$ (Krogh-Moe, 1965), $\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$ (Hyman, Perloff, Mauer & Block, 1967) and $\text{BaO} \cdot 4\text{B}_2\text{O}_3$ (Krogh-Moe & Ihara, 1969) all have structures consisting of frameworks built up from alternating pentaborate and triborate groups. These frameworks are very space-demanding, however, and a normal packing density of the atoms is achieved by the interpenetration of two separate borate anion frameworks. In $\text{K}_2\text{O} \cdot 3.8\text{B}_2\text{O}_3$, however, the borate anion forms a single framework. A normal packing density is here apparently achieved by an incorporation in the framework of BO_3 triangles and BO_4 tetrahedra. These additional units are perhaps crucial to obtaining the space filling required for the formation of a *single* framework consisting essentially of pentaborate and triborate groups. Each pentaborate group is now bonded to two triborate groups, one pentaborate group and a BO_3 triangle. The latter BO_3 triangle serves as a bridge to another triborate group. Each triborate group is bonded to two pentaborate groups, a BO_3 triangle and a BO_4 tetrahedron. This BO_4 tetrahedron similarly bridges to another triborate group.

The fraction of boron atoms in fourfold coordination should be $5/19 = 1/3.8 = 0.263$, according to the rule postulated by Krogh-Moe (1960). This rule is seen to be obeyed for the present structure. (Note that one of the fourfold-coordinated boron atoms, B(9), occupies a special position with half the multiplicity of a general position.)

The boron–oxygen bond lengths and bond angles are tabulated in Table 3. Reference can be made to Fig. 2, to identify the various bonds. The bond lengths show

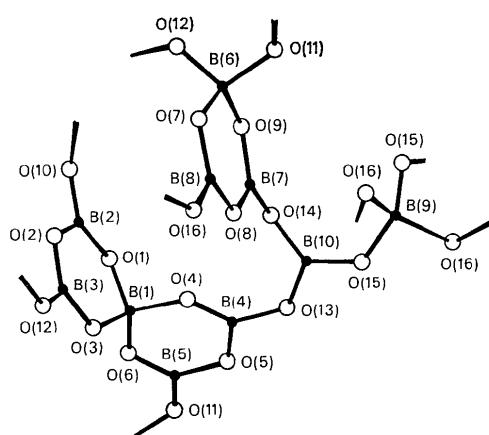


Fig. 2. Projection approximately along the b axis, showing the borate anion section included in the asymmetric unit. Open circles represent oxygen, filled circles represent boron. The numbering of the atoms is consistent with the tables.

Table 3. Interatomic distances and bond angles: boron–oxygen bond lengths (standard deviation 0.002 Å), potassium–oxygen distances below 3.5 Å (standard deviation 0.001 Å) and oxygen–boron–oxygen and boron–oxygen–boron bond angles (standard deviation 0.1°)

Distances listed for K(3) occur twice for each oxygen atom due to the symmetry centre.

B(1)—O(1)	1.494 Å	B(10)—O(13)	1.394 Å
B(1)—O(3)	1.459	B(10)—O(14)	1.372
B(1)—O(4)	1.465	B(10)—O(15)	1.336
B(1)—O(6)	1.464	K(1)—O(16)	2.682
B(2)—O(1)	1.341	K(1)—O(7)	2.723
B(2)—O(2)	1.373	K(1)—O(5)	2.732
B(2)—O(10)	1.382	K(1)—O(6)	2.855
B(3)—O(2)	1.396	K(1)—O(11)	3.054
B(3)—O(3)	1.364	K(1)—O(12)	3.060
B(3)—O(12)	1.345	K(1)—O(8)	3.117
B(4)—O(4)	1.336	K(1)—O(3)	3.245
B(4)—O(5)	1.381	K(1)—O(15)	3.367
B(4)—O(13)	1.377	K(2)—O(9)	2.681
B(5)—O(5)	1.404	K(2)—O(15)	2.748
B(5)—O(6)	1.360	K(2)—O(12)	2.749
B(5)—O(11)	1.346	K(2)—O(1)	2.799
B(6)—O(7)	1.464	K(2)—O(6)	2.820
B(6)—O(9)	1.469	K(2)—O(13)	2.857
B(6)—O(11)	1.479	K(2)—O(3)	2.875
B(6)—O(12)	1.465	K(2)—O(11)	2.926
B(7)—O(8)	1.378	K(3)—O(14)	2.789
B(7)—O(9)	1.347	K(3)—O(1)	2.805
B(7)—O(14)	1.366	K(3)—O(4)	3.120
B(8)—O(7)	1.355	K(3)—O(10)	3.262
B(8)—O(8)	1.399	K(3)—O(2)	3.315
B(9)—O(15)	1.479	K(3)—O(9)	3.428
B(9)—O(16)	1.460		
O(1)—B(1)—O(3)	110.4°	O(7)—B(8)—O(8)	120.4
O(1)—B(1)—O(4)	106.2	O(7)—B(8)—O(16)	124.1
O(1)—B(1)—O(6)	108.2	O(8)—B(8)—O(16)	115.5
O(3)—B(1)—O(4)	110.1	O(15)—B(9)—O(15)	112.0
O(3)—B(1)—O(6)	109.8	O(15)—B(9)—O(16)	103.9
O(4)—B(1)—O(6)	112.0	O(15)—B(9)—O(16)	112.3
O(1)—B(2)—O(2)	122.9	O(16)—B(9)—O(16)	112.6
O(1)—B(2)—O(10)	120.0	O(13)—B(10)—O(14)	118.7
O(2)—B(2)—O(10)	117.0	O(13)—B(10)—O(15)	116.1
O(2)—B(3)—O(3)	120.0	O(14)—B(10)—O(15)	125.0
O(2)—B(3)—O(12)	122.0		
O(3)—B(3)—O(12)	118.0	B(1)—O(1)—B(2)	120.5°
O(4)—B(4)—O(5)	121.6	B(2)—O(2)—B(3)	118.8
O(4)—B(4)—O(13)	123.2	B(1)—O(3)—B(3)	121.9
O(5)—B(4)—O(13)	115.2	B(1)—O(4)—B(4)	123.3
O(5)—B(5)—O(6)	119.9	B(4)—O(5)—B(5)	119.5
O(5)—B(5)—O(11)	115.1	B(1)—O(6)—B(5)	123.5
O(6)—B(5)—O(11)	125.0	B(6)—O(7)—B(8)	122.6
O(7)—B(6)—O(9)	112.0	B(7)—O(8)—B(8)	118.5
O(7)—B(6)—O(11)	109.2	B(6)—O(9)—B(7)	121.4
O(7)—B(6)—O(12)	108.8	B(2)—O(10)—B(2)	125.1
O(9)—B(6)—O(11)	106.1	B(5)—O(11)—B(6)	125.7
O(9)—B(6)—O(12)	111.5	B(3)—O(12)—B(6)	131.6
O(11)—B(6)—O(12)	109.0	B(4)—O(13)—B(10)	127.9
O(8)—B(7)—O(9)	122.9	B(7)—O(14)—B(10)	134.1
O(8)—B(7)—O(14)	119.7	B(9)—O(15)—B(10)	126.9
O(9)—B(7)—O(14)	117.2	B(8)—O(16)—B(9)	125.9

systematic variations, depending on adjacent boron–oxygen bonds. These variations were first brought to attention by Krogh-Moe (1972), and have since been

found in several anhydrous borates. In the present structure the pentaborate rings have two relatively short boron–oxygen edges, with boron–oxygen bond lengths of 1.336 Å [B(4)–O(4)] and 1.341 Å [B(2)–O(1)]. These bond lengths occur typically with threefold-coordinated borons, such as B(1) and B(4), bonded to one BO_4 tetrahedron and two BO_3 triangles. The opposite edges [B(3)–O(3)] and [B(5)–O(6)] of the pentaborate rings are longer (1.364 and 1.360 Å) due to the circumstance that the boron atoms B(3) and B(5) are each bonded to two BO_4 tetrahedra and only one BO_3 triangle. A similar asymmetry, though less pronounced, is seen for the triborate ring.

The intergroup bond angles [in the present case the boron–oxygen–boron bond angles for oxygens O(10) to O(16)] are distributed in the range 125.1 to 134.1°. This is a normal range for such bond angles. The boron–oxygen–boron in-ring bond angles are significantly smaller, however, ranging from 118.5 to 123.5°.

Only the potassium atom K(2) has a fairly well defined coordination shell, with 8 oxygen atoms in the range from 2.681 to 2.926 Å. (Table 3). No further oxygen atoms are found within a distance of 3.5 Å. The atoms K(3) (which occupies a special position at the origin) and K(1) do not have an obvious upper

limit for the coordination number. K(1) has 7 neighbours in the range from 2.682 to 3.117 Å and K(3) has 6 neighbours in the range from 2.789 to 3.120 Å.

Financial support of this work from the Norwegian Research Council for Science and Humanities and the technical assistance of Mrs I. Slaattelid is acknowledged.

References

- BORGREN, O. & MESTVEDT, B. (1973). *LSFVO 1*. Technical Report, Institutt for fysikalisk kjemi, NTH, Trondheim, Norway.
- GERMAIN, G., MAIN, P. WOOLFSON, M. M. (1971). *Acta Cryst. A* **27**, 368–376.
- HYMAN, A., PERLOFF, A., MAUER, F. & BLOCK, S. (1967). *Acta Cryst. B* **22**, 815–821.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- KROGH-MOE, J. (1960). *Acta Cryst. B* **13**, 889–892.
- KROGH-MOE, J. (1961). *Acta Cryst. B* **14**, 68–68.
- KROGH-MOE, J. (1965). *Acta Cryst. B* **18**, 77–81.
- KROGH-MOE, J. (1972). *Acta Cryst. B* **28**, 168–172.
- KROGH-MOE, J. & IHARA, M. (1969). *Acta Cryst. B* **25**, 2153–2154.
- ROLLET, A. P. (1935). *C. R. Acad. Sci. Paris*, **200**, 1763–1765.

Acta Cryst. (1974). **B30**, 1832

Thyroid Hormone Stereochemistry. I. The Molecular Structures of 3,5,3'-Triiodo-L-Thyronine (T_3) and L-Thyroxine (T_4)

BY ARTHUR CAMERMAN*

Departments of Medicine (Neurology) and Pharmacology, University of Washington School of Medicine, Seattle, Washington, U.S.A.

AND NORMAN CAMERMAN

Department of Biochemistry, University of Toronto, Toronto, Canada

(Received 14 November 1973; accepted 17 January 1974)

The crystal and molecular structures of the two thyroid hormones, 3,5,3'-triiodo-L-thyronine (T_3) and L-thyroxine (T_4) have been determined by X-ray crystallography. Crystals of T_3 hydrochloride trihydrate are monoclinic with $a = 29.080$, $b = 5.236$, $c = 17.047$ Å, $\beta = 115.85^\circ$, space group $C2$ with $Z = 4$. T_4 hydrochloride monohydrate also crystallizes in space group $C2$ with $a = 17.23$, $b = 5.14$, $c = 25.15$ Å, $\beta = 90.47^\circ$, $Z = 4$. Both structures were solved by Patterson and Fourier techniques and refined by full-matrix anisotropic least-squares methods. Final R values are 0.07 for T_3 and 0.107 for T_4 . In both T_3 and T_4 the two phenyl rings are not mutually perpendicular and mutually bisecting. Angles between the plane of the inter-ring ether linkage and the planes of the α - and β -phenyl ring planes are 90° and -13° respectively for T_3 and 101° and -34° respectively for T_4 . The four iodine atoms of T_4 are at the apices of a rather distorted tetrahedron. The conformation of the alanine side chain is very similar in both compounds. The conformation of T_3 is such that the 3'-iodine atom is *proximal* to the diiodo ring rather than *distal*; this conformation is opposite to that inferred from chemical studies. Theoretical calculations indicate this *proximal* conformation to be energetically favored over the *distal* one.

Introduction

The thyroid hormones L-thyroxine (T_4) and 3,5,3'-triiodo-L-thyronine (T_3) appear to exert an effect on nearly

every organ and tissue of the body. They are essential for normal growth and development and the control of oxidative metabolism, and have a profound effect on protein synthesis in many tissues. Although their biological importance is well established, the mechanisms of thyroid-hormone action remain largely obscure.

* Investigator of the Howard Hughes Medical Institute.