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The Direct Determination of the Crystal Structure of $NaB(OH)_4.2H_2O$

By S. Block and A. Perloff

National Bureau of Standards, Washington 25, D. C., U.S.A.

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The structure of $NaB(OH)_4.2H_2O$ has been determined by direct methods. Three-dimensional Cu $K\alpha$ single-crystal data were used. The space group is $P\bar{1}$, $Z=2$ and the cell dimensions are:

$a = 6{\cdot}126 \pm 0{\cdot}008$ Å $\qquad \alpha = 67°\ 55' \pm 07'$
$b = 8{\cdot}180 \pm 0{\cdot}008$ Å $\qquad \beta = 110°\ 35' \pm 07'$
$c = 6{\cdot}068 \pm 0{\cdot}008$ Å $\qquad \gamma = 101°\ 51' \pm 07'$

The structure consists of discrete tetrahedral $B(OH)_4^-$ groups and octahedrally coordinated sodium ions. An octahedron shares two edges to form chains parallel to the [100] direction. The chains are linked in the [001] direction by boron tetrahedra to form sheets parallel to the (010) face. Hydrogen bonds connect oxygen atoms within the sheet and link the sheets into a three-dimensional network. Bond distances and bond angles are presented and the application of the direct method is discussed.

Introduction

The structure determination of $NaB(OH)_4.2H_2O$ was undertaken for two reasons. One was to test the applicability of the general equation of Karle & Hauptman (1959) to the solution of the structure of a crystal of triclinic symmetry containing atoms of similar scattering power. The other was to further understanding of borate structural chemistry.

Experimental

The crystals were grown by adding an excess of sodium metaborate to a $0{\cdot}5N$ sodium hydroxide solution, warming to dissolve and then allowing this supersaturated solution to cool to room temperature. The cell parameters were determined with a calibrated precession camera. The cell dimensions* are

$a = 6{\cdot}126 \pm 0{\cdot}008$ Å $\quad \alpha = 67°\ 55' \pm 07'$ $\quad \varrho_o = 1{\cdot}743$ (Kemp, 1956)
$b = 8{\cdot}180 \pm 0{\cdot}008$ Å $\quad \beta = 110°\ 35' \pm 07'$ $\quad Z_c = 2{\cdot}001$
$c = 6{\cdot}068 \pm 0{\cdot}008$ Å $\quad \gamma = 101°\ 51' \pm 07'$

This cell was used during the course of this work and all work herein reported is on this basis.

The conventional unit cell obtained by the Delaunay reduction (Donnay & Nowacki, 1954) is:

$a = 6{\cdot}943 \qquad \alpha = 93°\ 11'$
$b = 8{\cdot}149 \qquad \beta = 125°\ 06'$
$c = 6{\cdot}126 \qquad \gamma = 105°\ 46'$

The transformation matrix to this new cell is

$$\begin{pmatrix} 1 & 0 & 1 \\ 0 & 1 & \bar{1} \\ \bar{1} & 0 & 0 \end{pmatrix}$$

Three-dimensional data were collected by the integrating Weissenberg method. The intensities were read on a densitometer. Lorentz and polarization corrections were applied by means of a program written for an IBM 704 computer. The data were placed on a single scale by correlation with a cross level. The crystal was of such dimensions that the maximum absorption correction was estimated to be less than 0·08. As photographic techniques were used, it was considered unnecessary to apply these corrections.

Structure determination

The first step was to calculate values of ε where $\varepsilon^2 = KF_0^2/\sum_i f_i^2$ and F_o = observed structure amplitude, f_i is the ith scattering factor and K is the value at the appropriate $\sin\theta/\lambda$ of the function which places the data on an absolute scale and corrects for the temperature motion. In order to remove the effect of overlap of atoms on the statistical distribution, only data for which $hkl \neq 0$ were used for the calculation of the K curve. Values of $\overline{|E|^2}$, $\overline{|E|}$, and $\overline{|E^2-1|}$ were calculated and are presented in Table 1. For space group $P\bar{1}$, ε and E are equivalent.

As can be seen by inspection of columns 2, 3, and 4 (Table 1), the presence or absence of a center of symmetry cannot be determined. The method proposed by Howells, Phillips & Rogers (1950) also gave ambiguous results. A piezoelectric test of the crystals

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* The uncertainties quoted on the cell dimensions are estimates based on past experience with the camera and measuring device used. In the authors' opinion a conservative estimate of error will be obtained if these uncertainties are treated as standard deviations.

Table 1. *Average values of* $|E|^2$, $|E|$, *and* $|E^2-1|$

	Theoretical F_c		$NaBO_2.4H_2O$ F_o		$Na_4P_4O_{12}.4H_2O$	
Average	Centro-symmetric	Non-centro-symmetric	Experimental	Corrected for extinction	F_o^2	F_c^2
$\|E\|^2$	1·0	1·0	0·970	1·054	1·0	1·04
$\|E\|$	0·798	0·886	0·819	0·818	0·833	0·838
$\|E^2-1\|$	0·968	0·736	0·869	0·987	0·875	0·934

was negative, and it was decided to begin the structure determination assuming a center of symmetry.

The values of ε' were computed from the integrated formula $(I_{2,0})$ (Karle & Hauptman, 1959)

$$(I_{2,0})=|\varepsilon'_H|^2-1=$$
$$\frac{2\sigma_2^2}{(C_1)^2\sigma_4}\left\langle\left(\frac{|\varepsilon_K|^t-1}{\log|\varepsilon_K|}-M\right)\left(\frac{|\varepsilon_{H+K}|^t-1}{\log|\varepsilon_{H+K}|}-M\right)\right\rangle_K$$

where t = integration range, chosen as 3,

$$\sigma_n=\sum_{i=1}^{N} f_i^n$$

N = number of atoms in the unit cell

$$M=\left\langle\frac{|\varepsilon_K|^t-1}{\log|\varepsilon_K|}\right\rangle_K=2\cdot90$$

and for $P\bar{1}$

$$2\sigma_2^2/(C_1)^2\sigma_4=1\cdot201\ .$$

It should be noted that any ε' can be calculated, even those outside the observed sphere of reflection. The reliability will depend on the number of contributors to the average value. Values of ε' were calculated for which no experimental ε was available. If the number of contributors was adequate and if the ε' was large, it was used for subsequent phase determinations.

A comparison of the values of ε' and ε showed a large apparent discrepancy for the $08\bar{1}$ reflection. Rechecking the original data disclosed a transcription error; the correct magnitude of ε $(08\bar{1})$ is 1·34 and not 2·96. The magnitude of ε' is 1·37. Thus the comparison can be a useful check of the data.

For the initial phase determining process, the integrated equation $(I_{3,0})$ (Karle & Hauptman, 1959) was used.

$$(I_{3,0})=\varepsilon'_{H_1}\varepsilon'_{H_2}\varepsilon'_{H_1+H_2}$$
$$=\frac{\sigma_2^3}{[C_1(t)]^3\sigma_4^{3/2}}\langle L_K L_{H_1+K} L_{H_1+H_2+K}\rangle_K-2\frac{\sigma_6}{\sigma_4^{3/2}}$$
$$+\frac{\sigma_8^{1/2}}{\sigma_4}(\varepsilon'_{H_1}\varepsilon'''_{H_1}+\varepsilon'_{H_2}\varepsilon'''_{H_2}+\varepsilon'_{H_1+H_2}\varepsilon'''_{H_1+H_2})+R'_{3,0}$$

where $L_H=(|\varepsilon_H|^t-1)/\log|\varepsilon_H|$; t = the integration range which was taken as 3; and the simplifying assumption was made that $\varepsilon'''\simeq\varepsilon'$. The remainder terms $(R'_{3,0})$ were ignored. Under these conditions the above becomes

$$(I_{3,0})=\varepsilon'_{H_1}\varepsilon'_{H_2}\varepsilon'_{H_1+H_2}=0\cdot4652\langle L_K L_{H_1+K} L_{H_1+H_2+K}\rangle_K$$
$$-0\cdot5973+0\cdot3151(|\varepsilon'_{H_1}|^2+|\varepsilon'_{H_2}|^2+|\varepsilon'_{H_1+H_2}|^2)\ .$$

Table 2. *Comparison of* $(I_{3,0})$ *and* $\varepsilon'\varepsilon'\varepsilon'$

H	$\varepsilon'(\sigma_{\varepsilon'})$	$\varepsilon'\varepsilon'\varepsilon'(\sigma_{\varepsilon'\varepsilon'\varepsilon'})$	$I_{3,0}(\sigma_{I_{3,0}})$
$0\bar{4}1$	1·42 (1·04)	2·89 (1·49)	2·43 (3·20)
$08\bar{2}$	1·43 (1·50)		
$04\bar{1}$	1·42 (1·04)		
$\bar{1}3\bar{2}$	−1·29 (0·99)	−2·47 (1·33)	−1·09 (2·71)
264	−1·49 (1·27)		
132	−1·29 (0·99)		
$21\bar{4}$	2·14 (1·10)	9·53 (1·53)	7·42 (3·37)
$2\bar{5}3$	2·32 (1·40)		
$4\bar{4}\bar{1}$	1·92 (1·23)		
$62\bar{2}$	1·44 (1·39)	2·95 (1·71)	1·20 (3·87)
$\bar{4}46$	−1·38 (1·50)		
264	−1·49 (1·27)		
$53\bar{1}$	1·62 (1·23)	4·64 (1·44)	2·60 (2·91)
$\bar{2}2\bar{2}$	1·75 (1·07)		
$35\bar{3}$	1·64 (1·20)		
$2\bar{1}2$	1·00 (1·03)	1·47 (1·47)	0·89 (3·08)
$\bar{4}2\bar{4}$	1·47 (1·48)		
$\bar{2}1\bar{2}$	1·00 (1·03)		
182	1·69 (1·33)	2·02 (1·59)	0·87 (3·45)
$2\bar{4}\bar{6}$	1·34 (1·36)		
$34\bar{4}$	0·89 (1·22)		
141	1·77 (1·00)	4·08 (1·42)	2·98 (2·86)
$4\bar{4}\bar{1}$	1·92 (1·23)		
500	1·20 (1·23)		
323	1·99 (1·12)	2·41 (1·28)	0·61 (2·46)
$\bar{1}2\bar{2}$	−1·08 (1·00)		
241	−1·12 (1·02)		
$21\bar{4}$	2·14 (1·10)	8·04 (1·47)	6·29 (3·02)
226	2·00 (1·33)		
432	1·87 (1·16)		

In Table 2 are presented ten randomly selected values of triple products calculated by the $I_{3,0}$ equation and by multiplying the appropriate ε' values. The standard deviations shown in the table were calculated by the following formulas, which assume perfect data without correlation (personal communication, J. Karle).

$$\sigma(\varepsilon'^2)=2N/D^{\frac{1}{2}}$$
$$\sigma(\varepsilon'\varepsilon'\varepsilon')=(\Sigma[\sigma(\varepsilon')]^2)^{\frac{1}{2}}$$
$$\sigma(I_{3,0})=(2N)^{3/2}/8^{\frac{1}{2}}D^{\frac{1}{2}}$$

where N = number of atoms in the unit cell = 16 and D = number of terms in the particular calculation.

In general the magnitudes computed by $(I_{3,0})$ are smaller than those of $\varepsilon'\varepsilon'\varepsilon'$. However, all values from $I_{3,0}$ and $\varepsilon'\varepsilon'\varepsilon'$ agree within one $\sigma(I_{3,0})$. The agreement of phases is excellent and is discussed in more detail below.

The possibility of rational dependence (Hauptman & Karle, 1959) was considered and a FORTRAN program was written for a high-speed electronic computer which obtained $\overline{|\varepsilon|^2}$ for all subsets described by means of a congruence of the form

$$ah+bk+cl=n(\text{mod } m)$$

where a, b, c, and the prime factors of m are integers ≤ 14. No strong rational dependence of this form was found. However, later it was seen that there is considerable overlap (Hauptman & Karle, 1962) in the Patterson synthesis and this, plus the extinction effects, probably accounts for the lack of better agreement.

The signs of $\overline{2}5\overline{3}$ ($\varepsilon'=2\cdot32$), 323 ($\varepsilon'=1\cdot99$) and $21\overline{4}$ ($\varepsilon'=2\cdot14$) were assumed positive and eventually the signs of 90 reflections were determined by utilizing the $I_{3,0}$ equation. A three-dimensional electron density map was calculated, but the structure was not readily apparent. In retrospect, it is clear that that the insufficient number of terms caused the peak heights to be incorrect and shifted from their true positions.

Of the 90 reflections used in the Fourier synthesis, the completed structure showed that 87 had the correct signs. The $|\varepsilon|$ values used were not the largest 90, but those which were readily calculated and gave seemingly consistent sign indications. They ranged in magnitude from 0·52 to 2·59 with 52 values above 1·5 and 80 above 1·0.

As it was not then known whether the inability to interpret the Fourier map was due to insufficient data, incorrect assumption of $P\overline{1}$ symmetry or the inability of the equation to give correct sign determinations, it was decided to compute a three-dimensional Patterson map and also to redetermine signs independently using the original probability method described in the A.C.A. monograph by Hauptman & Karle (1953) for the centrosymmetric case. Owing to considerable overlap the Patterson synthesis was not immediately interpretable. The structure was quickly solved by the original probability methods.

The relations

$$\Sigma_1=sE_{2H}=s\sum_{H}|E_H|^2-1$$

$$\Sigma_3=sE_H=s\sum_{ij}E_{H_i}(|E_{H_j}|^2-1),\ H=H_i+2H_j$$

gave encouraging sign determinations. After 39 signs were thus determined,

$$\Sigma_2=sE_H=s\sum_{K}E_{H_i}E_K,\ H=H_i+K$$

was used. In the early stages of the Σ_2 calculation, signs were compared with those calculated by equation ($I_{3,0}$) and found to be in good agreement. In order to obtain good resolution Σ_2 was used to obtain as many signs as possible. Of 632 E's with magnitudes $>0\cdot4$ the signs of 504 were thus determined. The electron density map obtained from these data was readily interpretable. The initial R value was 34%. The parameters were refined by the least-squares program of Busing & Levy (1959*a*) to $R=14\cdot9\%$. A comparison of the observed and calculated structure factors showed that the large F_o were consistently smaller than F_c. This indicated extinction effects. The intensities were corrected for secondary extinction by the simple method described by James (1954) where $I_{\text{corr}}=I_{\text{obs}}/(1-2gI_{\text{obs}})$. The extinction parameter was $g=0\cdot00045$. The intensity scale was such that the maximum correction was a factor of 4.

With the corrected data a difference map was made in an effort to locate hydrogen atoms. The resulting map contained more positive areas than the number of hydrogen atoms to be placed so that the result is not definitive. However, the hydrogen bonding suggested by the shortest oxygen to oxygen distances was corroborated by areas of positive electron density between all of the appropriate pairs of oxygen atoms. These positions were used as initial parameters for the hydrogen atoms in a final least-squares refinement.

Table 3. *Final atomic parameters*

Atom	x	y	z	B
Na	0·2412	0·1149	0·3692	1·61
O(1)	0·2120	0·2190	0·9214	1·32
O(2)	0·7640	0·4608	0·2661	1·10
O(3)	0·5610	0·3644	0·8375	1·12
O(4)	0·2210	0·3663	0·4879	1·09
O(5)	0·8158	0·0700	0·2213	1·77
O(6)	0·6691	0·1604	0·6088	2·04
B	0·3047	0·3728	0·7439	0·92
H(1)	0·69	0·12	0·09	3·7
H(2)	0·72	0·26	0·49	1·6
H(3)	0·71	0·41	0·15	2·9
H(4)	0·93	0·78	0·15	—*
H(5)	0·74	0·98	0·16	–*
H(6)	0·45	0·57	0·20	2·1
H(7)	0·06	0·39	0·42	–*
H(8)	0·39	0·82	0·28	3·0

* Indicates negative temperature factor, reset to $+0\cdot05$ for calculating structure factors.

With the data as corrected for extinction, the atomic parameters ultimately refined to give $R=11\cdot7\%$ (zero reflections omitted) and $R=13\cdot3\%$ (zero reflections included). The final coordinates are presented in Table 3. The observed and calculated structure factors are presented in Table 4.

Description of the structure

In the past this compound has been designated by formulas such as $Na_2O.B_2O_3.8H_2O$ and $NaBO_2.4H_2O$. On the basis of the present structural study, a more appropriate formula is $NaB(OH)_4.2H_2O$, and the compound can be designated as sodium tetrahydroxoborate dihydrate.

Table 4. *Observed and calculated structure factors*

ℓ	$\lvert F_o \rvert$	sF_c
	00ℓ	
1	155	-166
2	135	-138
3	57	-52
4	28	-27
5	25	20
6	37	-34
	10ℓ	
0	125	-110
1	116	104
2	270	391
3	174	-198
4	107	129
5	118	126
6	63	-62
	$10\bar{\ell}$	
1	160	-180
2	333	-353
3	260	309
4	30	-25
5	178	-217
6	31	28
7	0	5
	20ℓ	
1	320	405
2	83	71
3	62	-56
4	81	-68
5	0	9
6	77	81
	$20\bar{\ell}$	
1	22	-13
2	69	-68
3	153	-139
4	0	9
5	54	48
6	44	38
7	92	83
	30ℓ	
0	131	-136
1	176	-188
2	170	-183
3	141	159
4	28	-32
5	40	-33
	$30\bar{\ell}$	
1	72	64
2	225	293
3	25	-30
4	49	-48
5	116	123
6	83	-81
7	33	32
	40ℓ	
0	207	231
1	75	-81
2	0	11
3	0	3
4	24	-17
	$40\bar{\ell}$	
1	61	-53
2	34	-34
3	72	64
4	44	44
5	0	16
6	55	45
	50ℓ	
0	111	118
1	43	-28
2	37	26
3	69	-54
	$50\bar{\ell}$	
1	70	68
2	0	7
3	32	-21
4	44	-34
5	110	-112
6	49	54
	60ℓ	
0	79	-69
1	54	51
2	59	56
	$60\bar{\ell}$	
1	0	-13
2	92	-86
3	0	-16
4	32	23
5	33	29
	70ℓ	
0	51	-58
	$70\bar{\ell}$	
1	0	13
2	33	-27
3	23	-17
4	0	-12
	01ℓ	
1	163	102
2	191	250
3	206	262
4	153	-161
5	137	134
6	36	-30
7	72	-89
	$01\bar{\ell}$	
1	172	-136
2	174	-183
3	70	61
4	162	-169
5	101	88
6	0	0
	11ℓ	
0	63	-50
1	153	-176
2	0	26
3	99	-100
4	0	-5
5	123	124
6	0	-6
	$11\bar{\ell}$	
1	409	454
2	472	-559
3	94	-88
4	26	21
5	51	47
6	52	36
	$\bar{1}1\ell$	
0	248	290
1	114	105
2	179	-214
3	36	-23
4	140	147
5	68	-61
6	36	24
7	151	-129
	$\bar{1}1\bar{\ell}$	
1	106	100
2	246	293
3	58	-45
4	123	-125
5	62	-53
6	0	-4
	21ℓ	
0	315	-345
1	138	155
2	160	-179
3	64	-60
4	143	157
5	112	-110
6	28	-15
	$21\bar{\ell}$	
1	181	-188
2	52	52
3	24	21
4	369	360
5	96	-93
6	79	-75
	$\bar{2}1\ell$	
0	134	124
2	115	105
3	132	-120
4	64	52
5	212	-266
6	29	-22
7	99	90
	$\bar{2}1\bar{\ell}$	
1	110	-98
2	120	119
3	52	-41
4	129	121
5	0	10
	31ℓ	
0	238	248
1	156	156
2	62	-71
3	81	-67
4	89	-90
5	43	-34
	$31\bar{\ell}$	
1	347	-367
2	376	384
3	32	29
4	79	-69
5	0	-10
6	21	22
	$\bar{3}1\ell$	
0	196	-237
2	43	-36
3	0	-1
4	45	-40
5	66	57
6	0	10
7	72	74
	$\bar{3}1\bar{\ell}$	
1	91	71
2	62	60
3	24	21
4	58	52
5	50	-42
	41ℓ	
0	0	12
1	189	-200
2	166	191
3	92	77
4	53	-54
	$41\bar{\ell}$	
1	116	109
2	102	101
3	128	120
4	201	-250
5	0	-3
6	33	39
	$\bar{4}1\ell$	
0	66	-65
3	0	-29
4	118	-134
5	137	156
6	31	36
	$\bar{4}1\bar{\ell}$	
1	0	17
2	182	-220
3	43	36
4	29	-23
	51ℓ	
0	70	-70
1	0	13
2	29	31
3	57	46
	$51\bar{\ell}$	
1	179	210
2	211	-261
3	119	-122
4	49	44
5	32	45
6	21	11
	61ℓ	
0	32	-21
1	30	27
2	136	-135
	$61\bar{\ell}$	
1	27	-19
2	0	-10
3	39	-44
4	81	88
5	22	-24
	71ℓ	
0	20	27
	$71\bar{\ell}$	
1	139	-132
2	68	56
3	43	50
4	37	36
	02ℓ	
1	299	-366
2	338	-433
3	129	120
4	184	199
5	152	159
6	107	-91
7	41	38
	$02\bar{\ell}$	
1	290	202
2	239	-201
3	87	-72
4	63	50
5	61	-63
6	57	57
	12ℓ	
0	162	102
1	62	59
2	87	93
3	443	-394
4	123	115
5	0	9
6	59	-61
	$12\bar{\ell}$	
1	509	-465
2	44	-37
3	0	2
4	282	288
5	0	-7
6	37	26
	$\bar{1}2\ell$	
2	174	149
3	399	459
4	168	-185
5	0	-2
6	0	-8
7	67	65
	$\bar{1}2\bar{\ell}$	
1	224	198
2	366	-323
3	0	8
4	183	-191
5	96	86
	22ℓ	
0	45	-42
1	203	166
2	0	-7
3	237	-266
4	36	-16
5	44	-41
6	173	130
	$22\bar{\ell}$	
1	94	76
2	484	359
3	27	-29
4	37	-31
5	30	-13
6	0	-13
	$\bar{2}2\ell$	
0	118	-100
2	123	117
3	396	354
4	88	-84
5	118	-111
6	39	25
7	99	-100
	$\bar{2}2\bar{\ell}$	
1	69	-70
2	362	339
3	64	53
4	133	-125
5	0	16
	32ℓ	
0	57	-47
1	60	61
2	66	49
3	297	336
4	172	-158
5	106	-91
	$32\bar{\ell}$	
1	41	-33
2	74	72
3	58	72
4	102	-102
5	84	82
6	141	-123
	$\bar{3}2\ell$	
0	72	-67
1	240	237
2	22	21
3	444	-462
4	0	-19
5	153	-171
6	129	128
7	0	7
	$\bar{3}2\bar{\ell}$	
1	25	-15
2	156	161
3	113	-118
4	124	124
	42ℓ	
0	154	174
1	110	-108
2	0	-9
3	77	82
4	0	-15
	$42\bar{\ell}$	
1	85	83
2	249	-278
3	57	51
4	137	-123
5	26	-30
6	26	26
	$\bar{4}2\ell$	
0	91	-94
4	113	112
5	84	99
6	77	-85
	$\bar{4}2\bar{\ell}$	
1	61	-38
2	102	-112
3	120	118
4	89	103
	52ℓ	
0	158	-182
1	46	-36
2	41	42
3	95	-104
	$52\bar{\ell}$	
1	0	-12
2	0	-6
3	38	31
4	99	88
5	122	-124
	$\bar{5}2\bar{\ell}$	
2	130	-145
	62ℓ	
0	0	-16
1	42	46
2	0	-26
	$62\bar{\ell}$	
1	39	-28
2	141	154
3	157	-166
4	68	57
	72ℓ	
0	75	95
	$72\bar{\ell}$	
1	30	26
2	37	29
3	39	39
	03ℓ	
1	305	-248
2	126	126
3	367	-374
4	98	91
5	86	-88
6	35	30
7	49	53
	$03\bar{\ell}$	
1	405	303
2	62	-60
3	155	-150
4	152	144
5	0	-1
	13ℓ	
0	37	32
1	73	67
2	404	-362
3	47	51
4	92	84
5	82	-75
6	21	-13
	$13\bar{\ell}$	
1	369	250
2	227	174
3	64	-60
4	66	59
5	49	42
6	129	-120
	$\bar{1}3\ell$	
0	140	-126
2	398	449
3	102	108
4	0	16
5	109	113
6	55	-51
7	0	9
	$\bar{1}3\bar{\ell}$	
1	192	-192
2	31	28
3	121	121
4	83	-78
5	33	-26
	23ℓ	
0	310	246
1	412	326
2	89	-74
3	129	124
4	94	-83
5	0	-11
6	38	-39
	$23\bar{\ell}$	
1	126	-131
2	242	-206
3	89	85
4	66	-55
5	89	87
6	89	-96
	$\bar{2}3\ell$	
0	184	166
1	391	351
2	209	-189
3	252	267
4	176	-204
5	110	115
6	94	98
7	33	-29
	$\bar{2}3\bar{\ell}$	
1	266	-287
2	81	89
3	0	-9
4	161	-158
5	0	7
	33ℓ	
0	0	9
1	0	17
2	26	17
3	0	-19
4	0	18
5	142	125
	$33\bar{\ell}$	
1	122	-113
2	42	-30
3	88	94
4	85	-85
5	150	-135
	$\bar{3}3\ell$	
0	181	-173
1	462	477
3	85	90
4	98	93
5	137	-169
6	45	-49
7	0	-3
	$\bar{3}3\bar{\ell}$	
1	36	25
2	51	-46
3	47	35
4	101	93
	43ℓ	
0	154	-157
1	119	-109
2	206	212
3	57	-49
4	41	-43
	$43\bar{\ell}$	
1	117	-114
2	61	70
3	0	-14
4	51	43
5	23	-31
	$\bar{4}3\ell$	
0	74	77
1	136	-167
4	72	67
5	0	7
6	46	-41
	$\bar{4}3\bar{\ell}$	
1	194	249
2	62	-66
3	38	-25
	53ℓ	
0	33	-31
1	99	-108
2	34	-23
3	41	-37
	$53\bar{\ell}$	
1	177	187
2	63	54
3	96	-108
4	0	12
5	55	60
	$\bar{5}3\bar{\ell}$	
1	89	-90
	63ℓ	
0	30	32
1	65	63
2	119	-121
	$63\bar{\ell}$	
1	28	30
2	0	-23
3	35	32
4	47	49
	04ℓ	
0	428	-343
1	266	158
2	28	22
3	75	-84
4	109	108
5	85	-87
6	156	-161
7	56	51
	$04\bar{\ell}$	
2	28	-19
3	91	108
4	45	31
5	50	-44
	14ℓ	
0	66	63
1	410	415
2	234	-244
3	74	78
4	0	-2
5	30	-40
6	31	36
	$14\bar{\ell}$	
1	66	56
2	138	119
3	232	-235
4	37	-37
5	57	54
	$\bar{1}4\ell$	
0	228	173
1	313	-396
2	28	-30
3	141	-143
4	81	-77
5	82	88
6	45	-37
7	57	60
	$\bar{1}4\bar{\ell}$	
1	115	114
2	93	-89
3	127	132
4	41	-26
5	21	-21
	24ℓ	
0	226	210
1	192	-198
2	36	35
3	120	140
4	0	9
5	83	86
6	31	23
	$24\bar{\ell}$	
1	295	-251
2	47	33
3	0	-6
4	58	-38
5	0	13
	$\bar{2}4\ell$	
0	0	-3
1	289	-187
2	162	146
3	221	226
4	119	-118
5	95	-100
6	149	165
7	32	-22
	$\bar{2}4\bar{\ell}$	
1	239	-277
2	49	32
3	47	-38
4	57	55
	34ℓ	
0	45	38
1	119	-112
2	161	169
3	124	-139
4	49	-35
5	0	15
	$34\bar{\ell}$	
1	49	-49
2	180	-193
3	52	50
4	57	57
5	19	-17
	$\bar{3}4\ell$	
0	93	-81
1	149	145
2	15	-8
3	60	-51
4	100	93
5	48	56
6	124	142
7	68	-71
	$\bar{3}4\bar{\ell}$	
1	54	-45
2	105	105
3	85	-84
4	58	-55
	44ℓ	
0	137	-145
1	0	8
2	74	-74
3	39	-32
4	35	29
	$44\bar{\ell}$	
1	122	118
2	61	50
3	46	47
4	62	50
5	31	-46
	$\bar{4}4\ell$	
0	35	28
1	267	293
5	69	71
6	143	-159
	$\bar{4}4\bar{\ell}$	
1	0	4
2	84	-74
3	34	31
	54ℓ	
0	0	-18
1	134	127
2	43	-34
3	36	35
	$54\bar{\ell}$	
1	0	-19
2	45	46
3	27	24
4	20	-24
	$\bar{5}4\ell$	
0	35	35
	$\bar{5}4\bar{\ell}$	
1	111	128
	64ℓ	
0	44	36
1	0	-14
	$64\bar{\ell}$	
1	0	18
2	52	54
3	36	-44
	05ℓ	
0	37	14
1	170	-118
2	100	79
3	45	47
4	123	130
5	118	-119
6	0	-9
7	63	63
	$05\bar{\ell}$	
1	340	252
2	91	96
3	181	-185
4	29	-15
	15ℓ	
0	106	104
1	0	-1
2	87	-81
3	156	160
4	190	209
5	135	-135
6	27	26
	$15\bar{\ell}$	
1	234	-201
2	0	-9
3	125	-106
4	80	76
	$\bar{1}5\ell$	
0	300	-214
1	263	158
2	371	271
3	27	-20
4	346	-324
5	30	14
6	62	-62
7	69	63
	$\bar{1}5\bar{\ell}$	
1	88	85
2	69	59
3	67	58
4	37	-29
	25ℓ	
0	183	188
1	69	-61
2	129	-134
3	55	-50
4	61	-64
5	147	151
6	45	48
	$25\bar{\ell}$	
1	147	-140
2	65	-72
3	60	61
4	89	-81
	$\bar{2}5\ell$	
0	69	-68
1	50	36
2	185	-157
3	155	-149
4	70	-82
5	162	195
6	0	-11
7	78	-73
	$\bar{2}5\bar{\ell}$	
1	56	-42
2	0	-16
3	231	212
4	29	-29
	35ℓ	
0	139	-150
1	50	-45
2	76	85
3	71	-77
4	64	-63
5	71	67
	$35\bar{\ell}$	
1	107	106
2	92	-85
3	184	173
4	29	17
	$\bar{3}5\ell$	
0	232	229
1	30	-31
2	98	-104
3	28	-22
4	77	77
5	29	-25
6	66	76
7	0	19
	$\bar{3}5\bar{\ell}$	
1	157	-170
2	134	-135
3	27	-16
	45ℓ	
0	58	-65
1	155	165
2	0	10
3	61	-64
4	34	-28
	$45\bar{\ell}$	
1	102	97
2	26	23
3	73	-71
4	66	62
	$\bar{4}5\ell$	
0	24	-15
1	85	-78
4	134	179
5	98	-106
6	55	54
7	41	-40
	$\bar{4}5\bar{\ell}$	
1	0	2
2	90	86
3	73	78
	55ℓ	
0	28	32
1	26	-29
2	0	4
	$55\bar{\ell}$	
1	79	-81
2	138	138
3	56	-56
	$\bar{5}5\ell$	
0	63	-65
	$\bar{5}5\bar{\ell}$	
1	114	127
	06ℓ	
0	0	-8
1	154	167
2	48	54
3	0	5
4	57	57
5	42	-33
6	44	43
	$06\bar{\ell}$	
1	270	-226
2	27	26
3	26	-19
4	59	-47
	16ℓ	
0	169	-144
1	144	-131
2	90	-86
3	87	88
4	56	-52
5	81	82
6	62	61
	$16\bar{\ell}$	
1	64	64
2	55	54
3	36	36
4	148	-135
	$\bar{1}6\ell$	
0	0	8
1	44	36
2	51	54
3	20	-18
4	197	225
5	114	-126
6	40	-42
7	0	-8
	$\bar{1}6\bar{\ell}$	
1	29	19
2	52	43
3	58	-52
	26ℓ	
0	26	16
1	104	-93
2	40	-38
3	82	82
4	104	-106
5	0	-18
	$26\bar{\ell}$	
1	99	104
2	90	-90
3	0	7
4	88	74
	$\bar{2}6\ell$	
0	79	80
1	58	-53
2	294	169
3	167	-147
4	146	-172
5	0	-5
6	0	-7
7	84	82
	$\bar{2}6\bar{\ell}$	
1	171	158
2	97	-87
3	0	-2
	36ℓ	
0	154	152
1	0	14
2	0	-24
3	137	-130
4	67	60
	$36\bar{\ell}$	
1	73	59
2	34	-39
3	0	-9
	$\bar{3}6\ell$	
0	0	-15
1	70	-64
2	65	-65
3	98	90
4	183	-206
5	150	167
6	37	-36
7	69	-75
	$\bar{3}6\bar{\ell}$	
1	82	-72
2	25	22
3	120	114
	46ℓ	
0	67	-60
1	122	114
2	93	87
3	37	-39
	$46\bar{\ell}$	
1	100	-110
2	54	54
3	0	5
	$\bar{4}6\ell$	
0	0	10
1	120	111
2	259	-259
3	0	4
4	87	97
5	0	22
6	72	82
7	43	-35
	$\bar{4}6\bar{\ell}$	
1	44	-44
2	0	8
	56ℓ	
0	0	-21
1	17	18
	$56\bar{\ell}$	
1	47	-41
	$\bar{5}6\ell$	
0	53	-56
1	0	-22
2	107	110
3	0	3
4	186	203
5	141	-153
6	34	-40
7	57	65
	$\bar{5}6\bar{\ell}$	
1	0	16
	$\bar{6}6\ell$	
0	43	50
1	90	-84
2	104	115
3	25	-22
4	44	-45
5	43	38
6	28	-22
	$\bar{7}6\ell$	
3	32	33
4	135	-148
	07ℓ	
0	143	-146
1	103	-86
2	135	-127
3	339	300
4	117	-118
5	47	-38
6	65	67
	$07\bar{\ell}$	
1	63	-47
2	105	98
3	0	2
	17ℓ	
0	206	190
1	162	-156
2	45	-44
3	26	19
4	65	-68
5	29	-27
6	70	-75

Table 4 (*cont.*)

l	$\lvert F_o\rvert$	sF_c
	$17\bar{l}$	
1	26	18
2	87	-80
3	54	40
	$\bar{1}7l$	
0	159	-211
3	102	-107
4	20	23
5	0	19
6	146	150
7	0	9
	$\bar{1}7\bar{l}$	
1	0	13
2	0	4
3	65	-62
	$27l$	
0	46	45
1	24	-18
2	42	33
3	148	-148
4	129	131
5	33	28
	$27\bar{l}$	
1	61	49
2	40	39
3	35	32
	$\bar{2}7l$	
0	44	39
1	25	28
2	320	231
3	234	-172
4	130	141
5	46	42
6	127	-132
7	46	-52
	$\bar{2}7\bar{l}$	
1	32	-30
2	91	-82
	$37l$	
0	48	-46
1	115	123
2	95	94
3	39	-30
4	0	-11
	$37\bar{l}$	
1	27	-28
2	22	22
	$\bar{3}7l$	
0	235	243
1	88	-125
2	85	-80
3	0	-11
4	52	-44
5	56	46
6	43	-41
7	60	-63
	$\bar{3}7\bar{l}$	
1	0	17
2	0	17
	$47l$	
0	26	-23
1	0	-19
2	72	-67
	$47\bar{l}$	
1	25	33
2	0	-33
	$\bar{4}7l$	
0	40	-38
1	0	12
2	117	-111
3	125	124
4	65	-75
5	107	-117
6	38	28
7	22	28
	$\bar{4}7\bar{l}$	
1	0	-13
	$\bar{5}7l$	
0	130	-120
1	0	-12
2	51	-58
3	23	19
4	66	60
5	23	27
6	0	15
	$\bar{6}7l$	
1	37	37
2	117	118
3	26	-24
4	29	-22
	$08l$	
0	111	126
1	0	-3
2	105	-113
3	47	-47
4	78	-82
5	0	-11
6	87	96
	$08\bar{l}$	
1	111	-116
2	129	135
	$18l$	
0	35	21
1	135	-136
2	206	231
3	0	4
4	87	-82
5	0	4
	$18\bar{l}$	
1	0	-11
2	84	72
	$28l$	
0	51	-53
1	20	13
2	67	73
3	0	-3
4	30	37
	$28\bar{l}$	
1	193	216
2	101	-109
	$38l$	
0	46	-45
1	53	51
2	181	-200
3	94	121
	$38\bar{l}$	
1	17	-3
	$09l$	
0	32	38
1	57	58
2	62	78
3	54	52
4	115	-130
5	61	-77
	$09\bar{l}$	
1	17	-30
	$19l$	
0	20	-4
1	28	-22
2	32	13
3	72	76
4	30	-24
	$29l$	
0	80	-104
1	14	16
2	22	23
3	0	6
	$010l$	
2	89	88
3	20	40

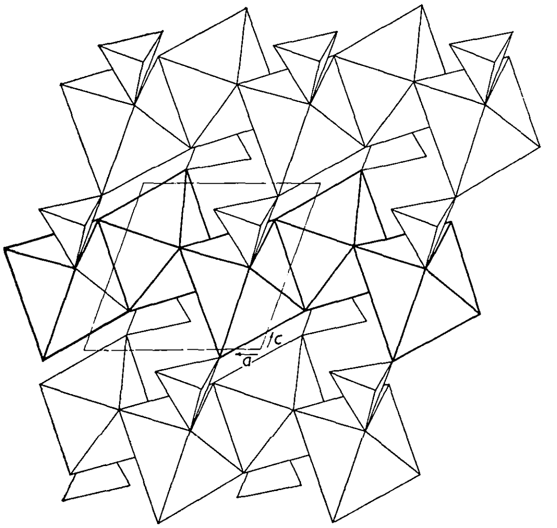

Fig. 1. The structure projected along the *b* axis. A chain of sodium octahedra is shown in heavy lines.

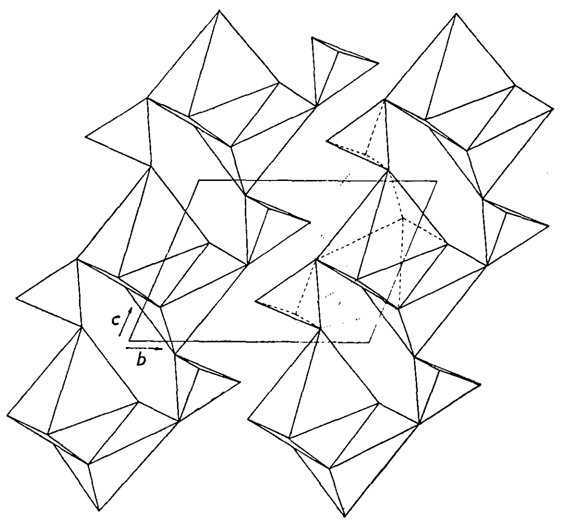

Fig. 2. The structure projected along the *a* axis. The crystallographically independent hydrogen bonds are indicated by dotted lines.

Table 5. *Bond distances and angles*

Boron tetrahedron	
B–O(1)	1·478 ± 0·005 Å
B–O(2)	1·479 ± 0·007
B–O(3)	1·477 ± 0·006
B–O(4)	1·474 ± 0·005
O(1)–O(3)	2·349 ± 0·005
O(2)–O(5)	2·463 ± 0·004
O(1)–O(2)	2·428 ± 0·005
O(2)–O(3)	2·452 ± 0·006
O(2)–O(4)	2·382 ± 0·005
O(3)–O(4)	2·392 ± 0·005
O(1)–B–O(3)	105·2 ± 0·4°
O(1)–B–O(4)	113·2 ± 0·4
O(3)–B–O(4)	108·3 ± 0·4
O(2)–B–O(4)	107·6 ± 0·4
O(2)–B–O(3)	112·1 ± 0·4
O(2)–B–O(1)	110·4 ± 0·4
Sodium octahedron	
Na–O(1)	2·474 ± 0·004 Å
Na–O(4)	2·458 ± 0·004
Na–O(5)	2·437 ± 0·002
Na–O(5)	2·480 ± 0·004
Na–O(6)	2·540 ± 0·004
Na–O(6)	2·371 ± 0·005
Na–Na	3·682 ± 0·004
O(2)–O(6)	3·332 ± 0·005
O(5)–O(6)	3·440 ± 0·005
O(4)–O(6)	3·235 ± 0·006
O(1)–O(6)	4·038 ± 0·005 Å
O(4)–O(1)	4·028 ± 0·005
O(4)–O(5)	3·334 ± 0·005
O(5)–O(6)	3·154 ± 0·006
O(1)–O(5)	3·303 ± 0·004
O(4)–O(5)	3·508 ± 0·004
O(5)–O(5)	3·260 ± 0·006
O(5)–O(6)	3·642 ± 0·005
O(6)–O(6)	3·372 ± 0·007
Hydrogen-bonded	
Linking sheets	
O(2)–O(3)	2·793 ± 0·005 Å
O(2)–O(4)	2·776 ± 0·005
O(2)–O(6)	2·669 ± 0·005
O(4)–O(3)	2·812 ± 0·005
O(6)–H(2)	1·0 ± 0·1
O(2)–H(3)	0·9 ± 0·1
O(3)–H(6)	0·5 ± 0·13
O(4)–H(7)	0·9 ± 0·1
O(5) and O(6) are in water molecules	
Within sheets	
O(5)–O(3)	2·904 ± 0·005 Å
O(5)–O(1)	2·764 ± 0·006
O(6)–O(1)	3·238 ± 0·005
O(6)–O(3)	2·827 ± 0·006
O(5)–H(1)	0·9 ± 0·1
O(1)–H(4)	0·8 ± 0·1
O(5)–H(5)	0·9 ± 0·1
O(6)–H(8)	0·9 ± 0·1

The structure consists of discrete tetrahedral $B(OH)_4^-$ groups and octahedrally coordinated sodium ions. Each slightly distorted sodium octahedron is formed from four water molecules and two hydroxyl groups. The hydroxyl groups belong to two different $B(OH)_4^-$ groups. An octahedron shares two edges, defined by pairs of centrosymmetrically related water molecules, with other octahedra to form chains parallel to the [100] direction (Fig. 1). The chains are linked in the [001] direction by boron tetrahedra. Each tetrahedron shares two of its corners with octahedra in adjacent chains, so that a sheet is formed parallel to the (010) face. Additional bonding within a sheet is provided by four of the eight crystallographically distinct hydrogen bonds. The remaining hydrogen bonds link the sheets into a three-dimensional network. The hydrogen bonds are indicated in Fig. 2. All of the hydrogen bonds within a sheet are of the OH–H_2O type. Of the four hydrogen bonds linking the sheets, three are OH–OH and one is an OH–H_2O bond. There are no H_2O–H_2O hydrogen bonds in the crystal.

The interatomic distances and angles as computed by the Busing & Levy (1959*b*) program are presented in Table 5. The four B–O distances are equal within the limits of error and the mean bond distance is $1{\cdot}476 \pm 0{\cdot}005$ Å. The tetrahedron is fairly uniform with angles ranging from 105·9° to 113·1°. The mean angle is $109{\cdot}5° \pm 2{\cdot}3°$.

The distances between hydrogen-bonded atoms are in the normal range, although O(1)–O(6) is appreciably longer than the others.

While the O–H distances cannot be considered accurate, they are all normal with the exception of O(3)–H(6). The 0·5 Å figure is not thought to represent a true interatomic distance, but it is suggestive of something different about that oxygen atom. If the proposed hydrogen bonding scheme is correct, then O(3) is peculiar in that it is involved in four hydrogen bonds as well as having a normal bond to a boron. It is hoped that a neutron-diffraction study on this crystal may be done in the future to locate the hydrogen atoms unambiguously.

It should be noted that this structure obeys the postulates proposed by Edwards & Ross (1960). The ratio of cation charge to total boron is one, and the boron exists in a discrete tetrahedrally coordinated form.

Conclusions

The equation $(I_{3,0})$ gave satisfactory phases for this structure. In general, the magnitudes computed by $(I_{3,0})$ are smaller than those of $\varepsilon'\varepsilon'\varepsilon'$. However, all values from $I_{3,0}$ and $\varepsilon'\varepsilon'\varepsilon'$ agree within one $\sigma(I_{3,0})$. Possible causes of the systematic deviations are (*a*) neglect of higher order correction terms (for example overlap in the Patterson syntheses), (*b*) assumption that $\varepsilon'^2 = \varepsilon'''\varepsilon'$, (*c*) crystallographic data which were deficient both in accuracy and perhaps in extent.

Of 250 calculations whose ε' values all corresponded to observed reflections, 242 gave correct sign indications. Of these 250 triple sum products only 15 gave a negative average value.

Of 465 triple sum products in which at least one ε' did not have an observed counterpart, 443 were correct, 12 wrong, 10 indeterminate and only 8 gave a negative sum. The totals are presented in Table 6.

Table 6

Number of triple sums calculated	715
Correct sign determination	685
Incorrect sign determination	20
Indeterminate	10
Negative	23

Of the incorrect sums, approximately 70% had fewer than the average number of contributors and about 60% had negative triple sums.

Of the 504 reflections obtained from the use of Σ_2 and included in the second electron density map, the signs of 359 of 364 with $|E| \geq 0{\cdot}7$, were correct while only 116 of 140 reflections with $0{\cdot}7 > |E| \geq 0{\cdot}4$ were correct. As only 83% of the phases of the reflections which have E magnitudes less than 0·7 were computed correctly (as compared with 98·6% for those E with magnitudes greater than 0·7) and furthermore as these smaller E values are less significant in the Fourier synthesis, it is probably not worthwhile to calculate these phases.

The relation Σ_2 should be used for the determination of the signs and as a constant check of previously determined signs. To obtain the original group of signs for Σ_2, either Σ_1 and Σ_3 or $(I_{3,0})$ can be used. Because it utilizes more data and is the same for all space groups, $(I_{3,0})$ is probably preferable.

After the errors due to extinction effects became apparent, the intensity data were corrected for this and new values of $\overline{|E|}$ and $\overline{|E^2-1|}$ were calculated (Table 1). The average values now agree very well with those expected for the space group $P\overline{1}$. However, this good agreement does not mean that quality of data is the only criterion for determination of a center of symmetry by statistical methods. The structure of the triclinic form of $Na_4P_4O_{12}.4H_2O$ has been carried out in this laboratory by Dr Helen M. Ondik (1963) and the original data also resulted in ambiguous average values. The structure determination resulted in the space group $P\overline{1}$, an R value of 8·6%, and no indications of extinction or absorption effects. Average values of $|E|$ and $|E^2-1|$ from the calculated structure factors still showed the ambiguity as to centrosymmetry (Table 1). This is another example (Hargreaves, 1955; Wilson, 1956) of the fact that the statistical determination of a center of symmetry should be used with caution.

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