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The Bond Lengths in the Sodium Metaborate Structure

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The position parameters of the sodium metaborate structure have been redetermined.

Each boron atom is bonded to one O_I atom with a bond length of 1·280 ± 0·016 Å and to two O_{II} atoms with B–O_{II} 1·433 ± 0·009 Å, while each sodium atom forms bonds with five O_I atoms and two O_{II} atoms, the Na–O distance ranging from 2·461 Å to 2·607 Å.

As previously found, the structure contains plane groups $(B_3O_6)^{-3}$ composed of three BO_3-triangles with two of three corners shared.

The large difference in the B–O bond lengths is attributed to an unequal distribution of the boron valence strength between the three bonds. Perfect valence balance requires a strength of 1·32 for the B–O_I bond and 0·84 for the B–O_{II} bond.

The early crystal structure studies of potassium metaborate (Zachariasen, 1937) and of the isomorphous sodium metaborate (Fang, 1938) established the existence of the group $(B_3O_6)^{-3}$ in the form of a plane ring of three BO_3-triangles.

The structure data reported for the sodium compound were:

	Rhombohedral	Hexagonal
Space group	$R\bar{3}c$	
Dimensions	$a = 7·22 \pm 0·01$ kX $\alpha = 111° 29'$	$a = 11·91 \pm 0·02$ kX $c = 6·45 \pm 0·01$ kX
N	6	18
All atoms in positions	6e	18e
Parameter values	X_r	$X_h = X_r - \frac{1}{4}$
Na	0·696 ± 0·003	0·446
B	0·362 ± 0·006	0·112
O_I	0·479 ± 0·006	0·229
O_{II}	0·138 ± 0·006	−0·112

Each O_I atom is bonded to five sodium and one boron atom, each O_{II} atom to two sodium and two boron atoms. Accordingly one oxygen atom is 'underbonded' and the other 'overbonded', and one would expect this imbalance in the bonding to result in appreciably different bond lengths for the two sets of oxygen atoms. However, the work of a quarter of a century ago was not sufficiently precise to detect such differences.

As part of the systematic studies of borate structures being carried out in this laboratory a redetermination has been made of the position parameters for $NaBO_2$, using new intensity data measured with a counter spectrometer.

The revised values for the cell dimensions are:

Hexagonal cell:

$$a = 11·925 \pm 0·001, \quad c = 6·439 \pm 0·001 \text{ Å}.$$

Rhombohedral cell:

$$a = 7·212 \text{ Å}, \quad \alpha = 111·54°.$$

In the following the hexagonal cell will be used.

Because there are no position parameters in the Z-direction, intensities were measured only for reflections $(HK0)$ and $(HK1)$ (using Cu $K\alpha$ radiation). The parameter refinement was carried out with the Busing–Levi IBM-704 program. The f-curve of McWeeny (1951) was assumed for boron, those of Berghuis *et al.* (1955) for sodium and oxygen. The 1938 parameters were used as starting values. Because of the incompleteness of the experimental data, the temperature factors were taken to be isotropic. A small secondary extinction correction was applied in the last refinement stage.

The least-square refinement, based on 53 reflections, gave a conventional R-factor (including zeros) of 0·067 and the parameter values listed in Table 1.

Table 1. *Position and thermal parameters for* $NaBO_2$

	X	B
Na	0·4371 ± 0·0004	1·77 ± 0·13 Å²
B	0·1234 ± 0·0012	2·24 ± 0·31
O_I	0·2307 ± 0·0006	1·77 ± 0·19
O_{II}	−0·1167 ± 0·0006	1·68 ± 0·20

(The hexagonal, X_h, and the rhombohedral position parameters, X_r, are simply related: $X_r = X_h + \frac{1}{4}$.) Table 2 gives the calculated and observed structure factors.

The interatomic distances calculated with the parameters of Table 1 are as follows:

B –1 O_I	1·280 ± 0·016 Å	Na–1 O_I	2·461 ± 0·009 Å
B –2 O_{II}	1·433 ± 0·009	Na–2 O_I	2·474 ± 0·002
O_I –2 O_{II}	2·383 ± 0·006	Na–2 O_I	2·607 ± 0·004
O_{II}–1 O_{II}	2·410 ± 0·013	Na–2 O_{II}	2·482 ± 0·006

Table 2. *Observed and calculated structure factors*

HKL	F_o	$0\cdot533F_c$	*HKL*	F_o	$0\cdot533F_c$
110	4·4	3·8	511	44·7	−45·9
300	5·7	5·4	431	30·2	29·7
220	5·8	−6·1	161	7·7	−7·3
410	12·9	−12·8	351	30·7	−29·7
330	82·2	−81·2	621	10·0	10·6
600	5·4	−5·0	541	3·7	−3·4
520	18·7	20·8	271	5·9	5·4
440	10·7	−9·3	811	7·7	−8·1
710	12·4	12·1	461	30·4	29·5
630	3·6	−3·7	731	6·5	6·6
550	6·7	−6·8	651	26·3	−27·0
900	70·7	76·9	191	4·5	4·2
820	1·5	−2·4	381	12·6	−12·6
740	nil	0·9	921	3·2	−3·8
660	30·7	−28·8	571	14·8	−12·9
10,1,0	10·4	−10·8	841	15·1	14·4
930	3·1	3·0	2,10,1	2·2	−0·9
850	4·9	−4·0	761	8·4	−8·5
12,0,0	6·5	6·6	491	3·8	2·8
11,2,0	7·4	−6·3	11,1,1	3·9	4·8
770	15·2	14·1	10,3,1	17·5	−15·0
10,4,0	7·0	−3·6	681	13·0	9·9
960	1·7	−1·8	951	nil	−0·1
211	3·1	−1·3	1,12,1	12·6	−11·0
131	55·6	−57·1	3,11,1	15·2	13·4
321	61·0	57·9	871	nil	0·5
241	50·3	48·3			

The B–O_I distance of 1·280 Å is the smallest, and the B–O_{II} distances of 1·433 Å are the largest values ever observed for the triangular boron–oxygen bond. The extreme values for the tetrahedral B–O bond length are 1·433 and 1·553 Å, and were found in β-HBO_2 (Zachariasen, 1963).

Were the valence strength of one for sodium equally distributed between the seven Na–O bonds, and were the valence strength of three for boron equally divided between the three B–O bonds, then the total bond strength for O_I would be 1·71 and for O_{II} 2·29, giving rise to a pronounced imbalance in the bond strength distribution. This great imbalance is in large measure removed by shortening (and hence strengthening) of the B–O_I bonds and a corresponding weakening of the B–O_{II} bonds.

It is reasonable to assume for small bond strengths that the bond length decreases linearly as the bond strength increases. However, because of the strong repulsive forces, it is to be expected that a slower decrease in bond length with increasing bond strength will occur at greater bond strength. One consequence of this departure from linearity between length and strength is that the mean interatomic distance will not be constant, but will increase with increasing fluctuations of individual bond distances from the mean. In $NaBO_2$ the mean B–O distance of 1·382 Å is appreciably higher than observed in other structures (1·365 Å) with smaller differences between individual bond lengths. Thus it is strongly indicated that there is appreciable departure from linearity between length and strength for the B–O bond at strengths above unity.

The mean length of the seven Na–O bonds is 2·512 Å. This should be compared with the value 2·45 Å usually observed for the Na–O bond when the coordination number is six. Accordingly one can, without appreciable error, assign a strength $s=0\cdot10$ to the long Na–O bond of 2·607 Å and a strength $s=0\cdot16$ to each of the other Na–O bonds.

In order to achieve detailed balance of valences the B–O_I bond of 1·280 Å must be ascribed a strength $s=1\cdot32$ and each bond B–O_{II} of length 1·433 Å a strength $s=0\cdot84$.

These results and the results from a number of other precisely determined borate structures were used to construct the empirical bond strength versus bond length relationship for the B–O bond reported in a recent article (Zachariasen, 1963).

Because only reflections *HK*0 and *HK*1 were used in the refinement, the *B*-values given in Table 1 will correspond to thermal vibrations essentially parallel to the plane of the $(B_3O_6)^{-3}$ group.

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