On the Crystal Structure of Hydrated Sodium Peroxoborate

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There is some controversy about the nature of the compound that crystallizes from a water solution of sodium borate and hydrogen peroxide. Thus it has been described both as $NaBO_2.H_2O_2.3H_2O$ and as $NaBO_3.4H_2O$.

The author obtained crystals of the compound from a solution of 3.5 g borax, 0.35 g NaOH and 9 ml 30 % H_2O_2 in 125 ml water. Analyses of the sodium, boron and active oxygen contents of the crystals were in agreement with the composition given by the above formulae. Weissenberg photographs were taken of two single crystals rotated around different axes. Comparison of single crystal photographs and powder photographs established that only one substance had crystallized from the solution. The intensities of 500 independent reflexions were estimated. The triclinic unit cell contains one formula unit $Na_2B_2(O_2)_2(OH)_4.6H_2O$ and has the dimensions a = 7.34 Å, b = 6.81 Å, c = 8.15 Å, with α = 101°, β = 110° and γ = 120°. The space group is P $\bar{1}$.

The structure has been determined by means of Harker-Kasper inequalities and three dimensional Patterson functions and has been verified by comparison of one calculated and one observed three dimensional electron density function. The unrefined parameters are given in Table 1.

There is one centrosymmetrical anion in the unit cell. The arrangement of the atoms is shown in Fig. 1. The bond distances and the bond angles in the negative ion are given in Tables 2 and 3. The B—O distances are in agreement with those reported earlier for tetrahedrally coordinated boron atoms [1]. The bond angles at the oxygen atoms and the bond distance within the peroxo group agree with the values reported for H_2O_2 [2]. The dihedral angle is 64° (Fig. 2).

The sodium ions are at symmetry centres of oxygen octahedra which share opposite edges. A part of the octahedral chains is shown in Fig. 3. Relevant bond distances are given in Table 4. The chains are parallel to the b-axis. The shared oxygen atoms

Table 1. The unrefined parameters of Na, O and B atoms.

	x	y	z
1 Na_1 in	0	0	0
1 Na_2 in	0	$\frac{1}{2}$	0
2 O_1 in	0.240	0.445	0.245
2 O_2 in	0.205	0.950	0.265
2 O_3 in	0.295	0.620	0.895
2 O_4 in	0.200	0.065	0.830
2 O_5 in	0.235	0.810	0.635
2 O_6 in	0.235	0.105	0.530
2 O_7 in	0.140	0.250	0.520
2 B in	0.120	0.930	0.615

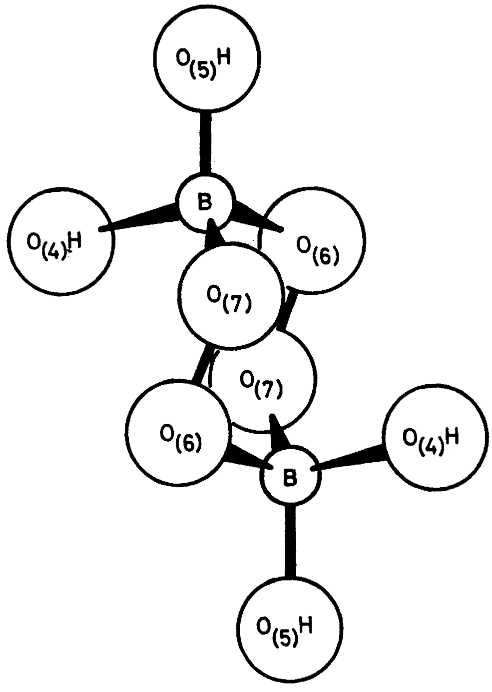

Fig. 1. The shape of the $B_2(O_2)_2(OH)_4^{2-}$ ion.

Table 2. Bond distances within the peroxoborate ion.

B — O_4	1.54 Å
B — O_5	1.44 Å
B — O_6	1.52 Å
B — O_7	1.42 Å
O_6 — O_7	1.47 Å

Table 3. Bond angles within the peroxoborate ion.

O_4-B-O_5	101°
O_4-B-O_6	116°
O_4-B-O_7	115°
O_5-B-O_6	104°
O_5-B-O_7	112°
O_6-B-O_7	108°
$B-O_6-O_7$	107°
$B-O_7-O_6$	107°

belong to water molecules. The sodium ions link the negative ions in the following way. In alternate octahedra in each chain, the two unshared oxygen atoms are incorporated in $O_{(4)}H$-groups from two negative ions. In every other octahedron each unshared oxygen atom forms part of a water molecule which is linked in turn by a hydrogen bond to an $O_{(5)}H$-group in a different negative ion.

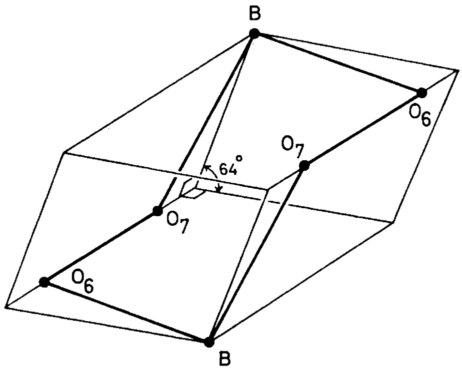

Fig. 2. The double peroxo bridge connecting two boron atoms.

The complete structure determination will be published when the refinement of the parameters has been completed.

Table 4. Bond distances between sodium and oxygen atoms.

Na_1-O_1	2.46 Å
Na_1-O_2	2.37 Å
Na_1-O_4	2.29 Å
Na_2-O_1	2.40 Å
Na_2-O_2	2.61 Å
Na_2-O_3	2.42 Å

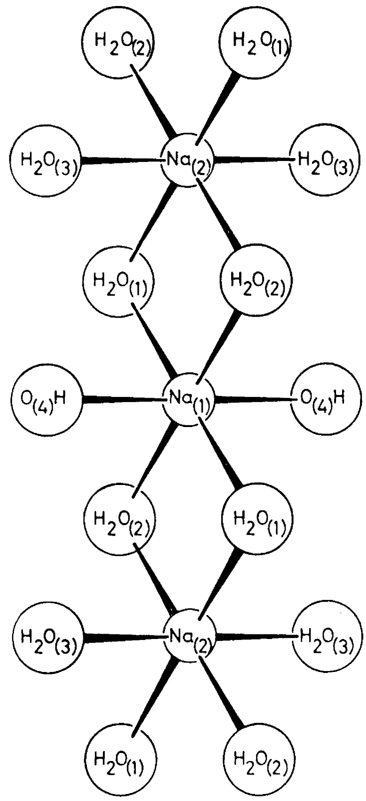

Fig. 3. Part of the chains of octahedra.

The author wishes to express his thanks to Prof. G. Hägg for all the facilities placed at his disposal, to Dr. I. Lindqvist for suggesting the problem and to Mr. Allan Brown for linguistic corrections of the manuscript. This investigation has been sponsored by grants from the *Nobel Foundation* and from *Anslaget till främjande av ograduerade forskares vetenskapliga verksamhet.* Facilities for the use of the digital computer BESK were granted by the Swedish Board for Computing Machinery.

1. Pauling, L. *The Nature of the Chemical Bond.* Cornell University Press, Ithaca, N. Y. 1960.
2. *Tables of Interatomic Distances and Configuration in Molecules and Ions,* The Chemical Society, London 1958.

Received May 12, 1961.