A New "Old" Sodium Boride: Linked Pentagonal Bipyramids and Octahedra in Na_3B_{20}**

Barbara Albert*

Few alkali metal borides can be considered to be well defined with regard to their composition and crystal structure. The reasons for this stem from difficulties in the synthesis and analysis of these compounds. First, it is difficult to carry out a reaction of the low-melting alkali metals with boron; second, the products often form microcrystalline powders instead of single crystals. The existence, composition, and structure of just one lithium–boron compound can be considered confirmed: Li_3B_{14}.[1] Two sodium borides have also been described, which will be discussed here, as well as potassium hexaboride, KB_6.[2]

Since boron-rich metal borides have interesting chemical, mechanical, and electronic properties, the lack of well-defined binary compounds in the system alkali metal/boron is unfortunate. Furthermore, the chemical bonding in these compounds is not fully understood. Additional motivation for these studies was the interesting structural chemistry of metal–boron compounds, which in its variety reflects the richness of the chemistry of boron-containing molecules.

Earlier, products of the reaction of sodium with boron were described as "NaB_6"[3] and NaB_{15}.[4] While the structure of NaB_{15} was determined from single-crystal data, the characterization of "NaB_6" remained unsatisfactory. Hagenmüller and Naslain prepared powders, the analysis of which indicated an approximate Na:B ratio of 1 to 6–7. The experimentally determined density was 2.11 g cm^{-3}. The powder diffraction pattern could not be indexed and differed from those of all other hexaborides, which crystallize without exception in the cubic CaB_6 structural type.[5]

We have now reproduced the synthesis of "NaB_6" from elemental sodium and boron. After removing the excess of sodium by distillation, we obtained bluish black powders[6] whose diffraction patterns were very similar to the one reported in the literature.[7] The product is air-sensitive and pyrophoric, which is not due to the presence of finely divided elemental sodium. This was proved by dispersing the sample in liquid ammonia, which did not turn blue.

The reflections of a high-resolution powder diffraction pattern[8] of the micro-crystalline product could be indexed in the monoclinic crystal system under the assumption that the unit cell is roughly three times larger than that of cubic CaB_6.[9] Relying on a relationship between the structures of "NaB_6" and CaB_6, we fixed the position of one Na atom analogous to that of the Ca atom in CaB_6 (Wyckhoff symbol 1*a*). The positions of all other atoms (first Na, then B) were localized by analyzing difference Fourier maps. It became clear that the structure, which was solved in the monoclinic space group *P*2/*m*, contains two additional mirror planes (perpendicular to [201] and [001] through the origin of the monoclinic unit cell). Therefore, a description in the orthorhombic system with an unit cell of twice the volume of a monoclinic cell is required.[10] The positions and thermal displacement parameters of the atoms were thus refined in the space group *Cmmm* (Figure 1).[11, 12]

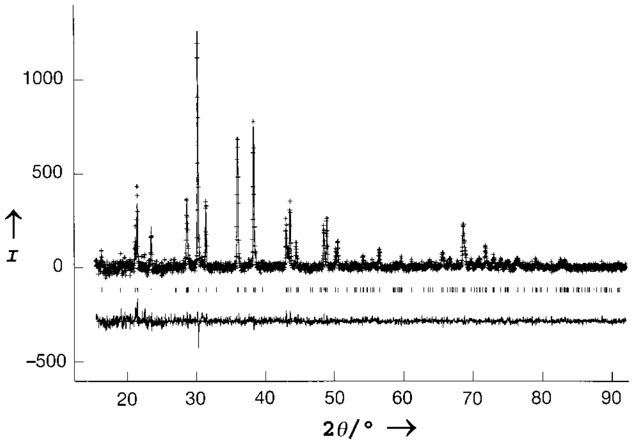

Figure 1. Observed (+) and calculated (solid line) powder diffraction pattern (corrected for the background) with the difference curve (bottom). The vertical dashes indicate the positions of reflections. I = intensity.

In the determination of the structure, two surprising discoveries were made. First, instead of the expected 18 boron atoms per monoclinic unit cell, 20 were localized. Therefore, the investigated compound is not NaB_6 (Na_3B_{18}) but Na_3B_{20}. Second, the occurrence of a pentagonal bipyramid consisting of seven boron atoms as a structural unit was proven for the first time by X-ray structure analysis. The boron framework in Na_3B_{20} thus is not composed entirely of linked octahedra, as in the hexaborides.[5] Figure 2[13] shows the arrangement of the polyhedra in a projection of the structure on the *ab* plane. A section of the structure of Na_3B_{20} (Figure 3) illustrates the position and the coordination of the sodium atoms in the cages of boron atoms.[14]

The mean boron–boron distances of 176 and 180 pm within the polyhedra and 171 pm between polyhedra are comparable to those in other boron compounds (e.g., Li_3B_{14}[1]). It is typical of boron-rich compounds that distances between atoms in the polyhedra are larger than those between them.

The compound first synthesized by Hagenmüller and Naslain in 1972 and known since as NaB_6 has been identified as a new sodium boride of composition Na_3B_{20} with an unusual crystal structure. The pentagonal bipyramid, which was previously detected in a few boron compounds by spectroscopic techniques, can now be regarded as a new structural unit in the domain of boron-rich compounds. The further characterization and analysis of the properties of this boride are currently under investigation.[15]

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[*] Dr. B. Albert
Institut für Anorganische Chemie der Universität
Gerhard-Domagk-Strasse 1, D-53121 Bonn (Germany)
Fax: (+49) 228-735660
E-mail: albert@snchemie2.chemie.uni-bonn.de

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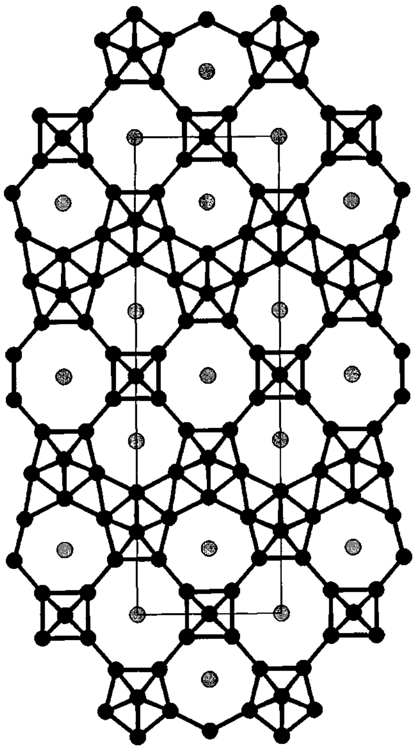

Figure 2. Projection of the structure of Na_3B_{20} on the *ab* plane (Na: light gray, B: dark gray, rectangle: unit cell).

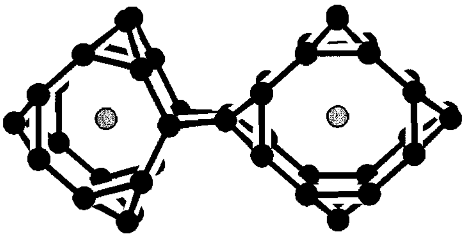

Figure 3. Section of the structure of Na_3B_{20} in the direction [001] (Na: light gray, B: dark gray). All boron atoms whose distance to a sodium atom is less than 340 pm are shown.

Experimental Section

Sodium (Merck, Darmstadt, p.a.) was refined by segregation and treated with boron (Chempur, Karlsruhe, 99.9+%) in a molar ratio of 1:1 at 1050 °C for 3 h in crucibles made of pyrolytic boron nitride, which were sealed in iron crucibles under helium by arc welding. The excess of sodium was removed by distillation at 10^{-2} mbar and 350 °C. The starting materials and products were handled under argon.

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[1] a) G. Mair, R. Nesper, H. G. von Schnering, *Mater. Sci. Monogr. (React. Solids, Part B)* **1985,** *28B*, 861 – 862; b) G. Mair, R. Nesper, H. G. von Schnering, *J. Solid State Chem.* **1988,** *75*, 30 – 40; c) Nesper and Wörle recently described two other lithium borides: M. Wörle, Dissertation, ETH Zürich, **1995**.

[2] R. Naslain, J. Étourneau, *C. R. Acad. Sci. Ser. C* **1966**, *263*(6), 484 – 487.

[3] P. Hagenmüller, R. Naslain, *C. R. Acad. Sci.* **1963**, *257*, 1294 – 1296.

[4] R. Naslain, J. S. Kasper, *J. Solid State Chem.* **1970**, *1*, 150 – 151.

[5] M. von Stackelberg, F. Neumann, *Z. Phys. Chem. B* **1932**, *19*, 314 – 320.

[6] Elemental analysis: Na 24.6 (by flame photometry), B 73.2 (titrimetric; boron is lost on dissolution in acid); calcd: Na 24.2, B 75.8. The absence of elements with atomic numbers higher than 11 was shown by EDX. The carbon and nitrogen content of the samples was less than 1% (Labor Pascher, Remagen).

[7] Powder diffraction patterns of our samples, which were prepared in iron ampoules with inner crucibles of pyrolytic boron nitride do not exhibit the reflection at about $2\theta = 44.1°$ which is present in the diffractograms of Hagenmüller and Naslain. It is probably the highest intensity reflection of $Fe_{23}B_6$ (PDF 34-0991).

[8] Huber powder diffractometer G645, quartz monochromator, $Cu_{K\alpha 1}$ radiation ($\lambda = 1.54056$ Å), flat-plate sample holder, measurement in transmission mode at 23.0(5) °C and 5×10^{-5} mbar, step width 0.004°, measurement range $\theta = 3 – 50°$.

[9] P. E. Werner, Program TREOR90, Stockholm, Sweden, **1990**

[10] In principle, powder diffraction data contain less information than single-crystal data. However, modern powder diffraction methods allow the solution of structural problems by investigating substances whose existence and structure could not be clarified earlier. In our case, it is not possible to decide between the monoclinic or the orthorhombic description of the structure on the basis of the convergence of the refinement. A possible monoclinic distortion is not resolvable. The necessary description of the structure in the orthorhombic crystal system with a large unit cell leads to slightly worse *R* values than when the structure is refined in the monoclinic crystal system. However, the composition and the structural arrangement of Na_3B_{20} have been proven to be independent of the crystallographic description and are unambiguous.

[11] A. C. Larson, R. B. Von Dreele, Program GSAS, Los Alamos, USA, **1985**.

[12] Structure refinement of Na_3B_{20}: orthorhombic, space group *Cmmm* (65), $a = 1869.45(6)$, $b = 570.09(2)$, $c = 415.06(1)$ pm, $\rho_{calcd} = 2.142$ g cm^{-3}, $Z = 2$, 135 reflections, 14 refined positional and thermal displacement parameters (all boron atoms were refined with a common thermal displacement parameter), $R_{wp} = 0.0871$, $R_p = 0.0666$, $\chi^2 = 1.172$, $D_{dw} = 1.767$, max./min. residual electron density 1.176/ – 1.002 e Å^{-3}. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-407159.

[13] R. Hundt, Program KPLOT, Bonn, Germany, **1979**.

[14] The coordination environment of one of the Na atoms can be described as a distorted cuboctahedron (coordination number 24); the second Na atom is coordinated by 20 B atoms.

[15] B. Albert, K. Hofmann, unpublished results.