NaB_5C: carbon insertion into a three-dimensional framework of boron octahedra leads to electron-precise cubic carbaborides

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The discussion of whether hexaborides need a minimum electronic stabilisation to exist or not, has now been enriched by the synthesis of NaB_5C, crystallising with the cubic CaB_6 structure.

Carbaborides are solids with an anionic framework consisting of linked boron polyhedra, which are electronically stabilised by the insertion of carbon. The name already indicates a similarity to polyhedral molecules, which are called carbaboranes: substitution of boron by carbon provides electrons which stabilise a certain polyhedral arrangement. Recently, we were able to synthesise a new ternary boron-rich compound, which crystallises in the cubic CaB_6[1] structure type, NaB_5C.

The existence of cubic alkali metal hexaborides has been discussed controversially for a long time. Two compounds, NaB_6[2] and KB_6,[3] have been reported. In an earlier work, we were able to show that 'NaB_6' should actually be described as Na_3B_{20},[4] which does not crystallise in the hexaboride structure type. According to Longuet-Higgins and de V. Roberts,[5] the reason for the instability of cubic hexaborides with monovalent cations is the electronic deficiency of their framework. Following traditional bonding concepts, derived analogous to Lipscomb's model for boron molecules, each B_6 octahedron needs twenty electrons: fourteen intramolecular, to fill the bonding molecular orbitals within the octahedra, plus six intermolecular to satisfy the 2 electron–2 center bond between neighbouring octahedra. This requirement of course is fulfilled for the electron-precise mother compound of the structure type CaB_6, but not for the alkali metal hexaborides, which are low in electrons. On the other hand, similar compounds with excess electrons, like LaB_6, are well known, the extra electron causing their metallic behaviour.

Looking for additional experimental evidence to illuminate the question of bonding and stability of hexaborides, we succeeded in synthesising a new compound. The reaction of a mixture of sodium, boron, and carbon at high temperatures[6] yields a crystalline powder, which contains carbon and shows the typical powder diffraction pattern of cubic hexaborides. The unprecedented combination of these two findings led to the assumption that carbon atoms are statistically distributed at the boron positions in NaB_5C. The substance is black and consists of crystallites similar to cubes and with edge lengths between 0.5 and 1 μm (Fig. 1). Electron energy loss spectroscopy (EELS) at several crystallite fragments proved a boron : carbon ratio of 5 : 1.

The crystal structure of NaB_5C was refined using X-ray powder data and the CaB_6 structure as starting model, boron and carbon sharing the 'framework positions' (Wyckhoff symbol 6f).[7,8] In Fig. 2, the fit between the observed data and the calculated diffraction pattern is shown. As was expected, the

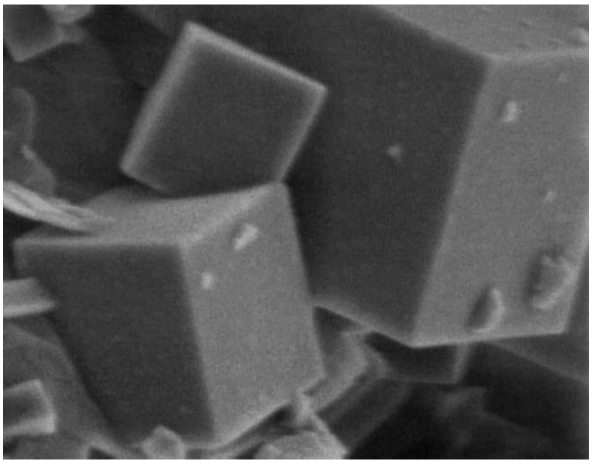

Fig. 1 Scanning electron micrograph of NaB_5C. The length of the edge of the crystallite in the front is 1 μm.

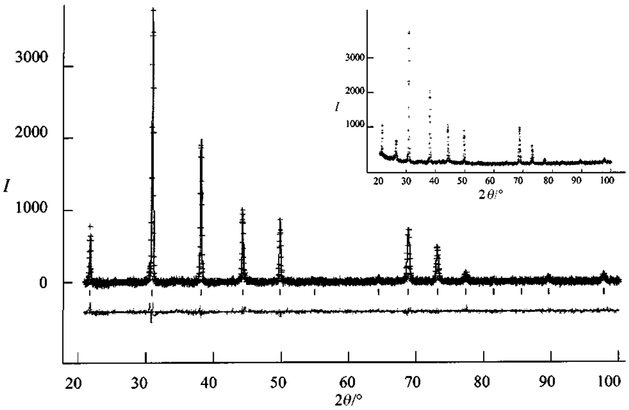

Fig. 2 Observed (+) and calculated (solid line) powder diffraction pattern (corrected for the background) with the difference curve (bottom). The vertical dashes indicate the positions of reflections. The uncorrected data are shown in the insert.

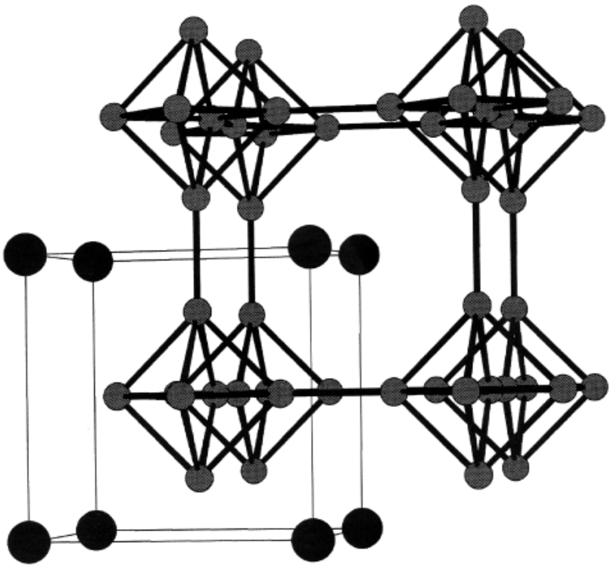

Fig. 3 Section of the structure of NaB_5C (Na: black, B/C: grey).

lattice constant of NaB_5C is smaller (4.09 Å) than the lattice constant which has been predicted for 'NaB_6'[9] (4.16 Å). In addition, we proved the mean B/C–B/C distance to be shorter than the mean B–B distance in hexaborides (1.706 Å in NaB_5C *versus* 1.736 Å in CaB_6[10]). Similar to other boron-rich compounds, the intramolecular bond distances within the octahedra are longer than the distances between them (1.716 Å *versus* 1.665 Å).

In conclusion, the new compound sodium hexa(carbaboride) exhibiting a cubic crystal structure (Fig. 3[11]) contains exactly the amount of carbon atoms in the anionic framework necessary to balance the electron deficiency of a hypothetical binary Na/B compound with a three-dimensional octahedral framework—one carbon atom per octahedron.

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6 Sodium (Merck, Darmstadt, p.a.) was refined by segregation and treated with boron (Chempur, Karlsruhe, 99.9+%) and graphite (Merck, Darmstadt) in a molar ratio of 6 : 5 : 1 at 1050 °C for 2 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 400 °C. The starting materials and products were handled under argon.

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8 Crystal data: NaB_5C, cubic, space group $Pm\bar{3}m$ (221), a = 409.25(1) pm, $V = 68.54 \times 10^6$ pm^3, $\rho_{\text{calc}} = 2.158$ g cm^{-3}, $Z = 1$, $\mu = 2.1$ mm^{-1}, 17 reflections, 3 refined positional and thermal displacement parameters (the boron and the carbon atom were refined with a common isotropic thermal displacement parameter), $R_{wp} = 0.0877$, $R_p = 0.0677$, $\chi^2 = 1.410$, $D_{\text{dw}} = 1.496$, $\rho_{\text{max}}/\rho_{\text{min}} = 0.854/-0.200$ e Å^{-3}. Reflections which stem from a small excess of graphite were cut out of the powder diagram before refinement. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-408930. Data were collected on a Huber powder diffractometer G645, with quartz monochromator, CuKα_1 radiation (λ = 1.54056 Å), flat-plate sample holder, measurement in transmission mode at 20.0(5) °C, 5×10^{-5} mbar, step width 0.006° Θ, measurement range 3–50° Θ. CCDC 182/1040.

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