The Structure Chemistry of Boron-Rich Solids of the Alkali Metals

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The electronic situation of boron atom frameworks in boron-rich solids is not easy to understand. Attempts to describe such compounds according to known bonding theories such as the Lipscomb or Zintl–Klemm approaches, are not completely unambiguous. To gain further insight and to create a solid experimental basis for the development of a conclusive bonding concept for non-molecular boron-rich compounds, it is essential to investigate metal borides in which the number of electrons transferred from the metal atoms to the boron atom framework appears to be well-defined. Alkali metal borides and carbaborides are such compounds, and it is the aim of this work to provide additional knowledge on their existence and crystal structures. Focussing on the crystal structures of alkali metal borides and carbaborides that are characterised by frameworks of interconnected boron atom polyhedra; it can be shown that there exist convincing geometrical similarities between boron-rich molecules and polyhedral entities in extended networks. This allows for the comparison between the bonding of boron-rich molecules with that of boron-rich solids.

Introduction

The chemistry of alkali metal borides has been covered by several reviews of Hagenmuller and Naslain and co-workers, that were published between 1967 and 1977.[1−3] At that time, it seemed likely that only three representatives of binary alkali metal borides had been synthesised in form of mono-phasic samples. These compounds were described as "NaB_6",[4] "NaB_{15}",[5,6] and "KB_6".[7,8] Unfortunately, the high-temperature synthesis conditions necessary to react boron and alkali metals usually do not lead to highly-crystalline products. The existence and crystal structures of the known boron-rich compounds of the alkali metals remained somehow unclear because in the sixties the technique of crystal structure solution and refinement based on powder diffractometry was still very young.

The lithium−boron(−carbon) system has been investigated by several groups. Boron-rich compounds like Li_3B_{14},[9−11] Li_2B_6,[9,12,13] and LiB_{13}[14] were found, as well as the lithium boride carbide LiBC.[9,15] Most of these borides were characterised by single-crystal X-ray diffraction. The formulae of these compounds were derived from the localisation and occupancies of the lithium ions in the crystal structures because it is very difficult to determine the exact composition of compounds consisting of light elements only. This was made even more difficult by certain disorder phenomena concerning the lithium atom positions. Therefore, it can be considered a real break-through, that due to the efforts of Nesper and von Schnering and co-workers we now know at least three well-defined representatives in the lithium−boron(−carbon) system. Other compounds which were described as "$LiB_{10.85}$",[16] "Li_2B",[17] "LiB",[18] "Li_5B_4", "Li_3B",[19,20] "Li_7B_6",[21] "LiB_2",

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Barbara Albert studied chemistry at the Rheinische Friedrich-Wilhelms-Universität in Bonn, Germany. She received her PhD in 1995, working with solid-state chemist Professor Dr. Martin Jansen. Thanks to a Feodor-Lynen-stipend from the Alexander von Humboldt foundation, Bonn, she spent a post-doctoral year in the group of Professor Dr. A. K. Cheetham at the Materials Research Laboratory, University of California, Santa Barbara, U.S.A., where she worked on Gismondine type (P) zeolites and their structural characterisation via powder diffractometry. From 1996 to 1998, she received a Lise-Meitner-stipend from the Land Nordrhein-Westfalen. Hereby enabled to develop her own research projects, she began to synthesise, characterise, and investigate new boron-rich compounds. In 1997, her habilitation project was awarded by the Ministry of Education and Science in Nordrhein-Westfalen with the Bennigsen-Foerder-award for young scientists and artists and in 1999 with the ADUC award. Since 1998, Barbara Albert has a C1 position as a scientific assistant with Professor Dr. J. Beck at the Justus-Liebig-Universität in Giessen.

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

"LiB$_{10}$",[22] and "LiB$_3$"[23] (in historical order) have not proven to give reproducible results with regard to their identity and properties.

Due to their well-defined oxidation state in chemical compounds, alkali metals are especially appropriate as reaction partners of boron to investigate the electronic situation of the boron framework in the resulting boron-rich solids. Today, modern powder diffractometry and solid-state NMR spectroscopy allow us to re-address the characterisation of alkali metal boron-rich compounds. It is necessary to carefully analyse the structure and electron count of boron atom polyhedra in well-defined compounds, in order to obtain a plausible description of the chemical bonding in boron-rich solids. An investigation into the geometrical similarities between the polyhedral entities in molecules and in solids is advisable before a comparison between the bonding situation in the two types of structures can be made. In this review, the chosen experimental system is that of the alkali metal boron-rich compounds. New compounds such as Na$_3$B$_{20}$,[24,25] NaB$_5$C,[26] Na$_2$B$_{29}$,[27] and KB$_5$C[28] will be described and put into context with what is known from earlier work on alkali metal borides and carbaborides. The electronic situation of these compounds will be compared with that of boron-rich molecules.

One question that is of great interest is: Does a monovalent sodium or potassium hexaboride exist? "NaB$_6$" and "KB$_6$" should be discussed on a new experimental basis. This point is very important for the discussion of the bonding in boron-rich solids. It should help to decide whether Lipscomb's bonding concept[29,30] developed for boron-rich molecules is applicable for non-molecular structures.

If hexaborides of type M^{I}B$_6$ do exist, the electronic analogy between octahedral [B$_6$H$_6$]$^{2-}$ molecules and octahedral [B$_6$]$^{2-}$ entities in the framework of boron-rich solids like CaB$_6$ cannot be made. According to the traditional picture which was first introduced by Longuet-Higgins and de V. Roberts[31] and which is depicted in Figure 1, each octahedron in the framework needs twenty electrons for stabilisation. Fourteen of these are needed to fill the molecular orbitals of the B$_6$ unity (multicentre bonds), and six (+6 from the bonding partners) are needed for the conventional 2electron-2center bonds directed outwardly towards neighbouring octahedra (the latter are comparable to the B–H bonds in the [B$_6$H$_6$]$^{2-}$ molecular anion). Eighteen electrons are provided by the six boron atoms, the missing two electrons have to be transferred from the cation to the framework. If the cation can provide even more electrons, like for example in LaB$_6$, the extra electron is obviously not needed for the bonding orbitals of the boron atom framework. This is shown by the high electrical conductivity that is observed for LaB$_6$. However, if the cations provide fewer electrons, the polyhedral arrangement should be destabilised. So, how could this be possible if compounds such as "NaB$_6$" or "KB$_6$" with an octahedral framework existed?

The correlation between crystal structure and electron count in similar compounds containing, for example, silicon or tin instead of boron, has been discussed before .[32–34]
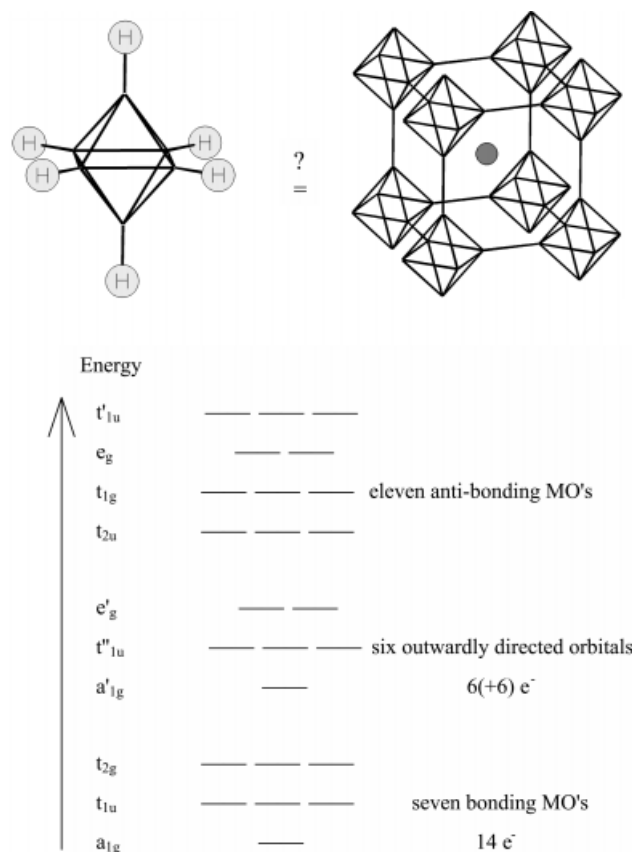

Figure 1. Cartoon showing a molecular [B$_6$H$_6$]$^{2-}$ anion (left) and the hexaboride structure model (right), bottom: MO scheme for the B$_6$ entity

The Alkali Metal Borides

Moissan (1892) and Kroll (1918) were the first to find indications for the existence of alkali metal borides when investigating "impure" samples of boron.[35,36] Forty years later, Hofmann[37] and later, Lipp[38] attempted to synthesise Li-B alloys, but they did not get well-defined compounds.

The first mono-phasic sample of an alkali metal boride described in the literature is a sodium boride synthesised by Hagenmuller and Naslain in 1963.[4] The formula "NaB$_6$" was assigned to the crystalline powder obtained by a high-temperature reaction from the elements. Today, we know the exact composition of this compound to be Na$_3$B$_{20}$.[24,25] It can be synthesised from the elements in arc-welded tantalum tubes lined with inner crucibles made of pyrolytic boron nitride at temperatures around 1050 °C. Its crystal structure recently was solved from high-resolution X-ray powder data and will be described below.

Since 1964, different groups have investigated both the lithium–boron and the potassium–boron systems. For the latter, only one representative could be synthesised in form of a crystalline powder, "KB$_6$".[7,8] It was obtained only from the α-rhombohedral modification of boron and its powder diffraction pattern suggested close similarity of the

crystal structure with that of the well-known alkaline earth hexaborides (Ca, Sr, Ba).[39−44] Alkaline earth hexaborides contain a boron atom framework of three-dimensionally interconnected octahedra and divalent metal ions in 24-fold coordination spheres between the octahedra (Figure 1, top right). However, recent results concerning "KB_6" using electron energy loss spectroscopy and solid-state NMR spectroscopy suggested the presence of a third element in this compound.[45] Therefore, it seems highly probable that no binary compound in the potassium−boron system has ever been prepared until now. With regard to the lithium−boron system, in 1964 the existence of "$LiB_{3.7−4.1}$" was suggested by Lipp.[38] Since then, most other lithium borides which have been described could not be characterised to a satisfying extent. Fortunately, about fifteen years ago Nesper and von Schnering and co-workers succeeded in growing single crystals of Li_3B_{14} and Li_2B_6.[9−13] Li_3B_{14} contains a boron atom framework of interconnected B_8 and B_{10} cages. For Li_2B_6, a boron atom arrangement similar to that of the alkaline earth hexaborides was found with two cations instead of one between the slightly distorted octahedra.

The first alkali metal boride that was obtained in the form of small single crystals was described as "NaB_{16}",[4] later the formula was corrected to "NaB_{15}".[5,6] Its crystal structure was published in 1970.[5] In fact, the analysis for these crystals published in the original paper already indicated a slightly different composition. This was confirmed by a recent reinvestigation of the crystal structure, using the combined capacity of different spectroscopic and diffraction techniques. These included X-ray and neutron powder diffractometry, ^{23}Na MAS-NMR spectroscopy, single crystal investigations, and electron microscopy. The actual phase composition is Na_2B_{29} and its crystal structure is characterised by a framework consisting of interconnected boron atom icosahedra and additional interstitial boron atoms.[27]

In conclusion, we now know of at least four examples of alkali metal borides which are well-defined in terms of their composition and crystal structures, and they are Li_2B_6,[13] Li_3B_{14},[11] Na_3B_{20},[24,25] and Na_2B_{29}.[27] Rubidium or caesium borides have not been obtained yet.

Alkali Metal Carbaborides

The alkali metal−boron−carbon system has not been investigated until recently, except for one compound discovered by Nesper and von Schnering and co-workers during their search for lithium borides, LiBC.[9,15] The crystal structure of LiBC is similar to that of hexagonal boron nitride, exhibiting planar 6^3-B/C-nets. The layers are stacked along the c axis with lithium ions in the centres of the formed hexagonal B/C prisms. Within the sheets and in between them, a colouring scheme characterised by strictly alternating B/C ordering is observed, similar to that found recently for another layer-type compound, CaB_2C_2.[46]

Formerly unknown carbaborides with three-dimensionally extended boron/carbon frameworks were discovered recently, NaB_5C and KB_5C.[26,28] These compounds, which are the first known representatives of ternary sodium and potassium B/C compounds, were obtained by a high-temperature reaction from the elements in form of monophasic crystalline powders without a detectable phase deviation. Their crystal structures resemble those of the alkaline earth hexaborides, carbon being statistically distributed at the boron atom positions of the octahedral framework. In fact, KB_5C is isoelectronic with the well-known CaB_6 and has similar properties.

At present, three representatives of the system alkali metal−carbon−boron are known. These are LiBC, NaB_5C, and KB_5C.

Crystal Structures of the Boron-Rich Compounds of Alkali Metals

The crystal structures of NaB_5C, KB_5C, Li_2B_6,[13] Na_3B_{20}, Li_3B_{14},[11] and Na_2B_{29} are shown in Figure 2.[47]
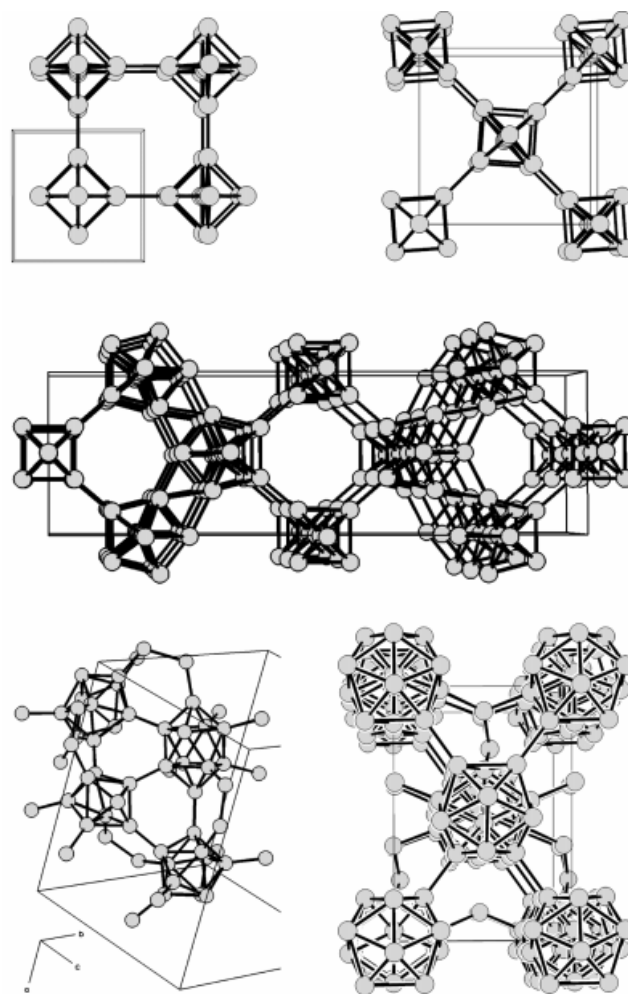

Figure 2. Perspective views of the unit cells of NaB_5C (top left), Li_2B_6 (top right, view along [001]), Na_3B_{20} (middle, view along [001]), Li_3B_{14} (bottom left, only a portion of the unit cell contents is shown for reasons of clarity), and Na_2B_{29} (bottom right, view along [010])

Table 1. Structure data on boron-rich solids of the alkali metals

Compound	ref.	Space group	Lattice parameters [pm,°]
Li_2B_6	[9,12,13]	*P4/mbm*, no. 127	597.5, 418.9
Li_3B_{14}	[9,10,11]	*I-42d*, no. 122	1076.4, 894.7
LiBC	[9,15]	*P6_3/mmc*, no. 194	275.2, 705.8
Na_3B_{20}	[24,25]	*Cmmm*, no. 65	1869.5, 570.1, 415.1
Na_2B_{29}	[27]	*I1m1*, no. 7	585.9, 1039.9, 833.2, 90.4
NaB_5C	[26,28]	*Pm-3m*, no. 221	409.3
KB_5C	[28]	*Pm-3m*, no. 221	412.8

Structural data of these phases is summarised in Table 1. The crystal structures of alkali metal boron-rich compounds are characterised by non-metal frameworks consisting of different polyhedra that are three-dimensionally interconnected. Metal ions are localised in the cavities between the polyhedra. The interatomic distances are shorter than the intramolecular distances within the polyhedra. This is a well-known phenomenon and occurs due to the deficiency of electrons in the multicentre bonds in the boron atom clusters relative to the 2electron-2center bonds between them. Table 2 gives the averaged different inter- and intramolecular B-B distances for alkali metal borides.

The polyhedra observed in these compounds are as follows: octahedra in NaB_5C, KB_5C, and Li_2B_6,[13] octahedra and pentagonal bipyramids in Na_3B_{20}, dodecahedra and bicapped quadratic antiprisms in Li_3B_{14},[11] and icosahedra in Na_2B_{29}. Most of these polyhedra are slightly distorted, this will be discussed later.

In the cubic carbaborides, the B/C framework maintains the high symmetry of the hexaboride structure, whereas in Na_3B_{20} a less symmetric but otherwise very similar arrangement of polyhedra is present in which two-thirds of the octahedra are replaced by pentagonal bipyramids. Ribbons of these pentagonal bipyramids run parallel to the b axis of the unit cell. These ribbons are formed because only four of the seven boron atoms of a pentagonal bipyramid form 2electron-2centre bonds with four neighbouring polyhedra (two octahedra, two pentagonal bipyramids), similar to the hexaboride structure. Each of the remaining three boron atoms per polyhedron shows close contact to two boron atoms of neighbouring polyhedra. The boron atom coordination spheres of the sodium cations are 20-fold and 24-fold, respectively. This is shown in Figure 3.

The 24-fold coordination sphere is very similar to that of the cations in the carbaborides.
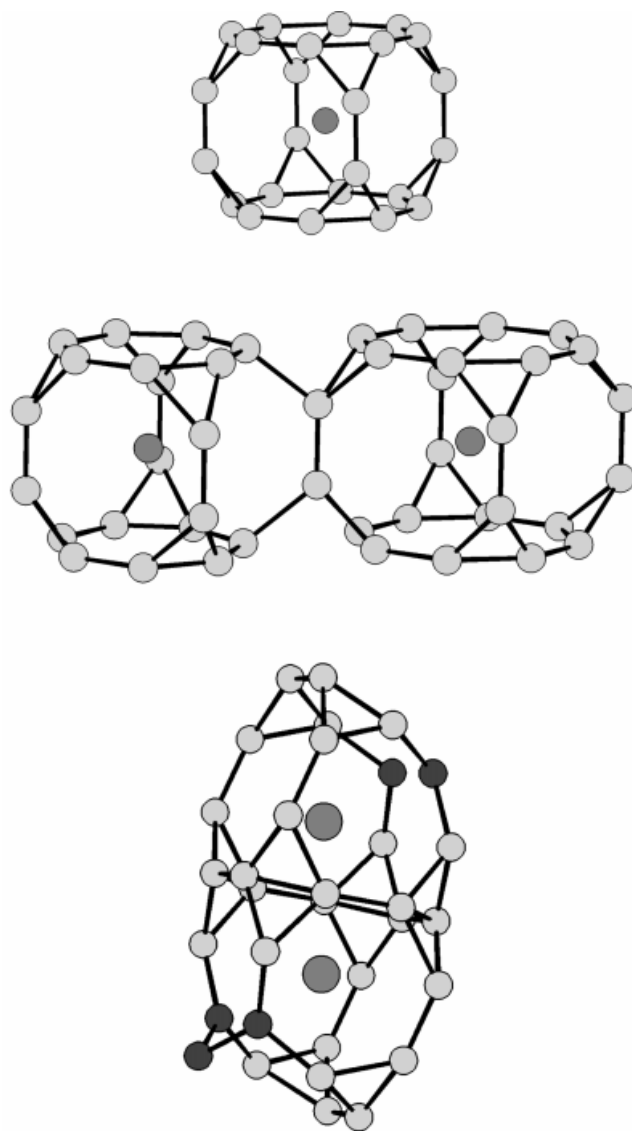

Figure 3. Sections of the structures of NaB_5C (top), Na_3B_{20} (middle), and Na_2B_{29} (bottom); sodium atoms are light grey, boron atoms are dark gray (polyhedral) and black (interstitial)

Na_2B_{29} was formerly known as "NaB_{15}", and the slight difference in the two types of sodium atoms with respect to their boron atom coordination sphere, eventually led to the proper compositional description of this compound (Figure 3, bottom). Using ^{23}Na-MAS triple quantum NMR spectroscopy the presence of two types of sodium atoms

Table 2. Inter- and intramolecular B−B distances for solids and intramolecular B−B distances for molecules

Polyhedron	Molecule: mean intrapolyhedral B−B distance [pm]	Solid: mean intrapolyhedral B−B distance [pm]	Solid: mean interpolyhedral B−B distance [pm]
$[B_6]$	$K_2[B_6H_6]$:[50] 172	Li_2B_6:[13] 176	171
	$[N(CH_3)_4]_2[B_6H_6]$:[63] 169	Na_3B_{20}: 177	172
$[B_7]$	$[(C_5H_5N)_2CH_2][B_7Br_7]$:[51] 174	Na_3B_{20}: 180	171
$[B_8]$	$[Zn(NH_3)_4][B_8H_8]$:[52] 177	Li_3B_{14}:[11] 180	174
$[B_{10}]$	$[N(C_2H_5)_3H]_2[B_{10}H_{10}]$:[53] 178.5	Li_3B_{14}:[11] 181.5	174
$[B_{12}]$	$[N(CH_3)_4]_2[B_{12}H_{12}]CH_3CN$:[54] 178.5	Na_2B_{29}: 182	177

with distinct boron atom environments was detected. The different coordination spheres of the sodium atoms are as a result of the presence of two types of interstitial boron atoms close to a single type of sodium atom in one case, and the presence of only one type of interstitial boron atom close to the second type of sodium atom in the other. The coordination sphere of Na1 includes 20 neighbouring boron atoms with a mean Na−B distance of 284 pm, whereas Na2 coordinates 21 boron atoms with a mean distance of 286 pm. Due to the loss of symmetry, the crystal structure of "NaB$_{15}$" = Na$_2$B$_{29}$ originally described in the orthorhombic crystal system, had to be refined in the monoclinic crystal system.

Polyhedra in Boron-Rich Solids and Molecules

In order to compare the bonding situation of boron atom polyhedra in solids with that in molecules, it is first necessary to compare their geometric situations. Boron atom cages have been found in the *closo*-hydroborates [B$_n$H$_n$]$^{2-}$ with n = 5−12.[48] For such compounds with n = 6, 8, 9, 10, 11, and 12, single crystal X-ray structure determinations have been performed and the overall regularity of these polyhedra was confirmed. Homoatomic polyhedra in boron-rich systems are always isohedral containing only n = 3 polygons (deltahedra), as can be seen in Figure 4.
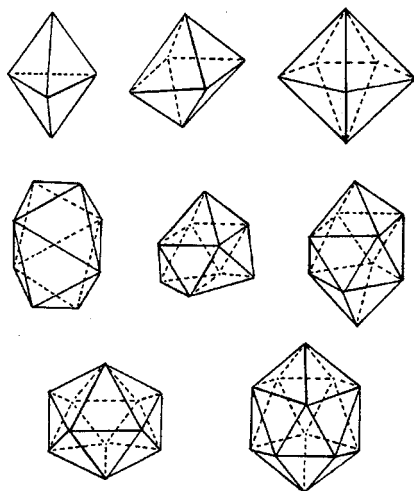

Figure 4. Polyhedra in *closo*-hydroborates according to Barton[48]

However, these polygons do not necessarily have to be regular. In principle, the octahedron and icosahedron are regular (Platonic) solids, the trigonal and pentagonal bipyramids have been described as semi-regular (Catalan) solids.[49] Less regular is the n = 8 cluster, which is a bisdisphenoid called a triangulated dodecahedron, the n = 9 and n = 10 cluster are monocapped and bicapped antiprisms, the n = 11 polyhedron is called an octadecahedron. Five of these polyhedra known from *closo*-hydroborates and their derivatives, can also be found in alkali metal boron-rich solids, the octahedron, pentagonal bipyramid, dodecahedron, bicapped antiprism, and the icosahedron. Data on the B-B bond lengths are given in Table 2 already indicate a comparability of the polyhedral entities in solids and molec-
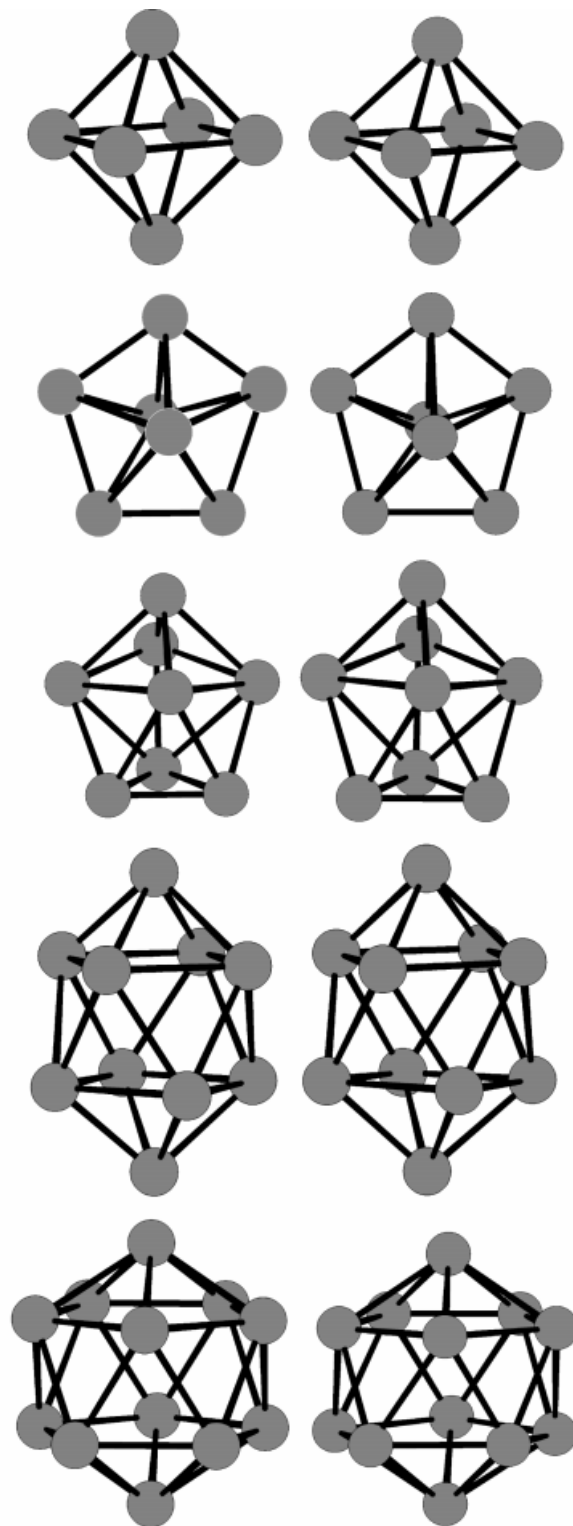

Figure 5. Comparison of the polyhedra found in *closo*-hydroborates (left, top to bottom: K$_2$[B$_6$H$_6$], [(C$_5$H$_5$N)$_2$CH$_2$][B$_7$Br$_7$], [Zn(NH$_3$)$_4$][B$_8$H$_8$], [N(C$_2$H$_5$)$_3$H]$_2$[B$_{10}$H$_{10}$], [N(CH$_3$)$_4$]$_2$[B$_{12}$H$_{12}$]·(CH$_3$CN) and alkali metal borides (right, top to bottom: Na$_3$B$_{20}$, Li$_3$B$_{14}$, Na$_2$B$_{29}$)

ules. Their similarity can be appreciated in Figure 5, where the same polyhedra extracted from the crystal structure descriptions of K$_2$[B$_6$H$_6$],[50] [(C$_5$H$_5$N)$_2$CH$_2$][B$_7$Br$_7$],[51] [Zn-(NH$_3$)$_4$][B$_8$H$_8$],[52] [N(C$_2$H$_5$)$_3$H]$_2$[B$_{10}$H$_{10}$],[53] and [N-

Table 3. Degree of polyhedral distortion (r.m.s.) for different boron cages in molecules and solids

Polyhedron	Point group	Molecule: r.m.s.	Solid: r.m.s.
$[B_6]$	O_h	$K_2[B_6H_6]$:[50] 0, $[N(CH_3)_4]_2[B_6H_6]$:[63] 0	KB_5C: 0
			Na_3B_{20}: 0.0155
			Li_2B_6:[13] 0.0128
$[B_7]$	D_{5h}	$[(C_5H_5N)_2CH_2][B_7Br_7]$:[51] 0.0502	Na_3B_{20}: 0.0820
$[B_8]$	D_{2d}	$[Zn(NH_3)_4][B_8H_8]$:[52] 0	Li_3B_{14}:[11] 0.0170
$[B_{10}]$	D_{4d}	$[N(C_2H_5)_3H]_2[B_{10}H_{10}]$:[53] 0.0042	Li_3B_{14}:[11] 0.0465
$[B_{12}]$	I_h	$[N(CH_3)_4]_2[B_{12}H_{12}]CH_3CN$:[54] 0.0045	Na_2B_{29}: 0.0506

$(CH_3)_4]_2[B_{12}H_{12}]CH_3CN$[54] are compared with those extracted from alkali metal borides.

Deviations from the ideal (which in principle cannot exist: by definition, an octahedron is an ideal octahedron or it is not an octahedron[55]) are quantified using the Program SYMMOL,[56] which is based on the idea, that symmetry can be treated "as a continuous property rather than a discrete ("yes or no") one".[57] Table 3 summarises a comparison between molecular boron atom cages and cages cut out from extended boron atom frameworks, by giving the r.m.s. (root mean square) values which characterise the degree of distortion of the polyhedra. These values are always higher than zero when crystallographic symmetry is not present.

Besides the first trivial case (top, crystallographic symmetry is already O_h), it is obvious that the polyhedra are more distorted in compounds with extended frameworks than in molecules. However, the "ideal" symmetry of the polyhedra is clearly determined even for the more distorted entities and the deviations from regular polyhedra are quite small.

Conclusions

At present, the alkali metal−boron system and the alkali metal−boron−carbon system are characterised by the proven existence of seven representatives. By crystal structure analyses of these compounds, a class of well-defined boron-rich solids has been established. These compounds are especially useful in the analysis of the bonding situation in electron-deficient polyhedral *frameworks*. Lipscomb's concept is usually applicable in describing the bonding situation in electron-deficient boron-rich *molecules*. It states that for molecular B_n *closo*-cages, the electronic demand necessary to stabilise the polyhedral arrangement is $2n + 2$, according to the traditional counting scheme (Rudolph−Williams−Wade rules[58−60]). Even if we have to remind ourselves that there exist other concepts to describe boron-rich compounds (for example Mingos' rules[61]) and of known exceptions from Lipscomb's predictions (for example B_9Br_9[62] and $Li_{1.8}B_{14}$[9−11]), the conclusions which can be drawn from the experimental findings summarised in this review are as follows. The analysis of the crystal structures of alkali metal borides and carbaborides reveals geometrical similarities between polyhedra in boron-rich solids and boron-rich molecules, which suggest a comparability of their bonding situation. Consequently, each octahedral B_6 entity which is part of an extended framework should need $2n + 2$ (= 14) electrons plus six electrons for the interpolyhedral contacts, as it was suggested 45 years ago by Longuet-Higgins and de V. Roberts. Within their limitations, the evidence described above confirm the applicability of this concept, since compounds correctly described by the formulas NaB_6 and KB_6 were found not to exist. Instead, we discovered NaB_5C and KB_5C, for which the electron count is fulfilled.

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