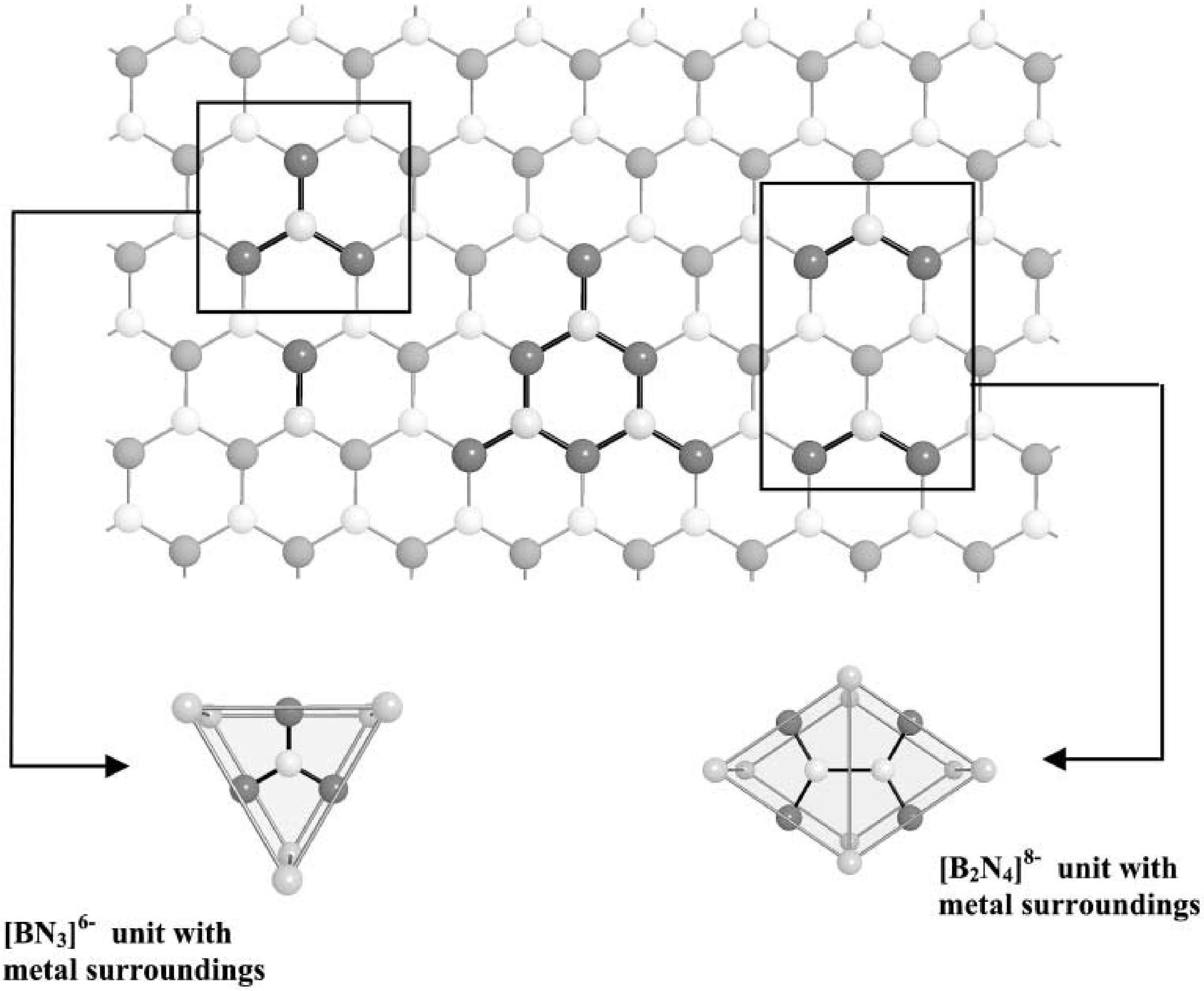
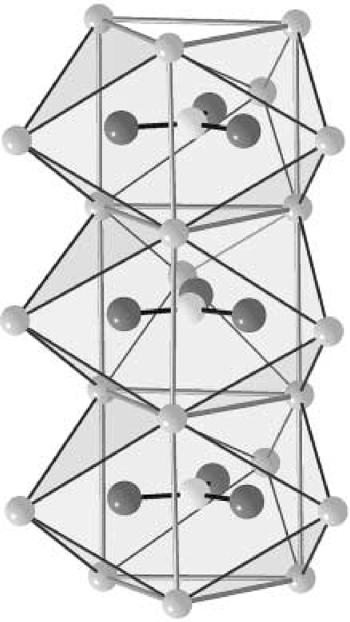
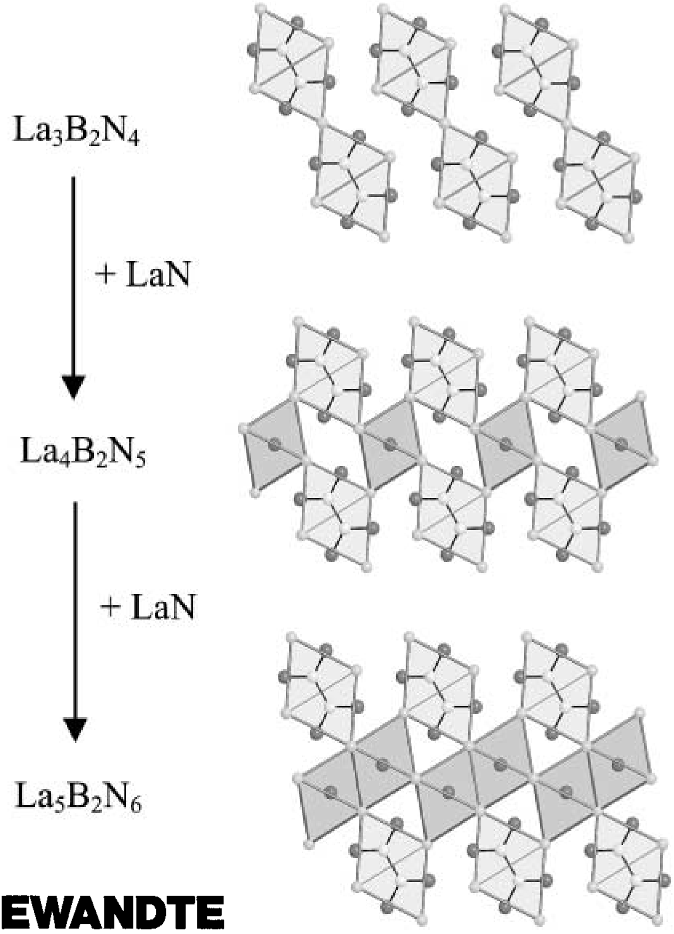




$[La_{6/2}La_3(BN_3)]$ column from $La_6(B_3N_6)(BN_3)N$



Nitridoborates of the Lanthanides: Synthesis, Structure Principles, and Properties of a New Class of Compounds

Björn Blaschkowski, Haipeng Jing, and H.-Jürgen Meyer*

Investigations of the nitridoborates of lanthanides (Ln) have progressed significantly during the last few years. New compounds have been synthesized and characterized and are presented here together with some of their properties. Currently two distinct methods serve for the preparation of nitridoborate compounds; either hexagonal boron nitride undergoes a fragmentation through the reaction with LnN, or dinitridoborate ions are converted into other nitridoborate ions. Lanthanide nitridoborates contain molecular anions such as $[BN]^{n-}$, $[BN_2]^{3-}$, $[B_2N_4]^{8-}$, $[B_3N_6]^{9-}$, and $[BN_3]^{6-}$ which may occur in combinations with other nitridoborates or with additional nitride ions. In crystal structures of lanthanide nitridoborates these anions are arranged in layers and are surrounded by metal atoms in a characteristic fashion. Terminal N atoms are capped by metal atoms forming a square-pyramid, and B atoms prefer a trigonal-prismatic environment of metal atoms. Nitridoborates form saltlike as well as metal-rich compounds and have the potential to show a lot of what are considered to be important solid-state properties, thus they have a good chance to establish their position within the group of relevant materials.

1. Introduction

The discovery of new materials always raises hopes for improved or combined material properties. Many metal borides and nitrides are chemically, thermally, and mechanically very stable or show good electrical conductivities. What should one therefore expect for ternary compounds in the system metal – B – N?

The first nitridoborate compounds known were Li_3BN_2 and alkaline-earth metal (E) compounds of the type $E_3(BN_2)_2$, the BN_2 anions of which were characterized by vibrational spectroscopy.[1] Several years later single-crystal X-ray investigations were reported for Li_3BN_2[2] and $Sr_3(BN_2)_2$.[3] The alkaline-earth-metal nitrides E_3N were tested (as well as alkaline-earth metals) as catalysts for high-pressure conversions of hexagonal boron nitride (h-BN) into its cubic modification. Because alkaline-earth-metal nitrides (and alkaline-earth metals themselves) react with h-BN to form nitridoborates, the nitridoborates are believed to be particularly important in this conversion as they can form an eutectic mixture with BN.[4, 5] Since then, numerous phase equilibria in the ternary system metal – B – N have been examined, also in regard to this application.[6, 7]

The elements B and N show different coordination geometries in structures. In metal borides the trigonal-prismatic arrangement of metal atoms about the boron atom dominates. In metal nitrides the nitrogen atom is surrounded predominantly octahedrally by metal atoms. A similar picture becomes apparent for the structural preferences of the anions in the system metal – B – N.

For ternary metal – B – N compounds the different interactions between metal and boron, metal and nitrogen, as well as boron and nitrogen have to be considered. Depending on the type of the metal atoms we can distinguish three groups of metal – B – N compounds which are presented here.

1.1 Boride – Nitride Compounds of the Transition Metals

Transition metals are known to form numerous stable binary boride and nitride compounds. However, combinations of transition metals with boron and nitrogen are rare. Solid-state reactions between Ti powder and BN yield TiN and TiB_2.[8] Reactions of metal borides with nitrogen, or of metal nitrides with boron lead to compounds similar to alloys with a low degree of substitution.[9]

Boride – nitride compounds contain no bonds between B and N atoms. Their structures of the formula type M_2BN ($M = Mo$, Nb)[10] combine structural characteristics typical of

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metal borides and metal nitrides. As in numerous metal nitride compounds the nitrogen atoms occupy octahedral holes (Figure 1), the boron atoms typically reside inside a trigonal-prismatic arrangement of metal atoms. In addition, the boron atoms are arranged to form infinite kinked chains ($B{-}B = 184$ pm in Nb_2BN). Similar chains of boron atoms are known from structures of CrB[11] and FeB.

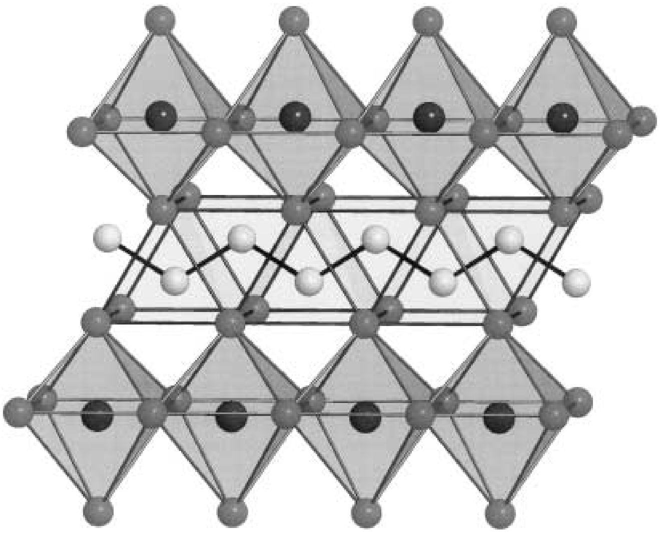


Figure 1. Section from the structure of Nb_2BN with N atoms (black) in the octahedral holes and the trigonal-prismatic arrangement of Nb atoms (gray) around the B atoms (white).

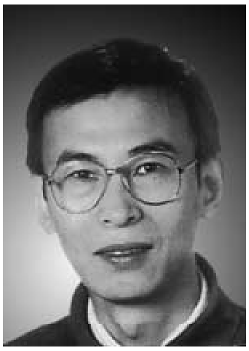
1.2 Nitridoborates of the Alkaline and Alkaline-Earth Metals

Alkaline and alkaline-earth metals form saltlike compounds with the linear dinitridoborate ion.[12] The $[NBN]^{3-}$ ion contains $B{=}N$ bonds with bond lengths of approximately 135 pm and is isolectronic to $[C_3]^{4-}$($C{-}C$ bond length 135 pm in $Ca_3Cl_2C_3$[13] and 133 pm in Mg_2C_3[14]), $[CBN]^{4-}$ ($C{-}B$ bond length 144 pm, $B{-}N$ bond length 138 pm in Ca_3Cl_2CBN[15]), and CO_2. Among the simplest examples of compounds with dinitridoborate ions are Li_3BN_2,[2] Na_3BN_2,[16] and compounds with the general formula $E_3(BN_2)_2$ with E = Ca, Sr, Ba[3, 17–19] and Eu[20] (Figure 2).

The two known phases for Li_3BN_2 differ only by the relative arrangements of their Li^+ and $[BN_2]^{3-}$ constituents. When α-Li_3BN_2 is heated to 862 °C it transforms into β-Li_3BN_2 which melts at 916 °C.[21] Na_3BN_2 was prepared through a high-pressure synthesis. Nitridoborate–nitride compounds of the type $E_3(BN_2)N$ are verified for E = Mg[22] and Ca.[23] $Mg_3(BN_2)N$ can be transformed into a high-pressure modification, with a structure (space group *Pmmm*)[24] topologically identical to the structure of $Ca_3(BN_2)N$ (space group *P*4/*mmm*) shown in Figure 2.

Björn Blaschkowski, born 1965 in Cologne, studied chemistry in Tübingen, where he finished his degree in 1998 with work on high-temperature superconductors. Afterwards he worked in the group of Professor Sibylle Kemmler-Sack on the development of HTSL bands then in 1999 joined the group of Professor H.-Jürgen Meyer at the Institute for Inorganic Chemistry in Tübingen. There he is working on his PhD thesis in the field of syntheses and characterization of ternary and quaternary nitridoborates.

B. Blaschkowski



H. Jing

H.-J. Meyer

Haipeng Jing, born 1953 in the P.R. of China, studied chemistry first at the Northwest University of Xi'an in China, then at the University of Tübingen in Germany. From 1997 to 2001 he worked on his PhD thesis entitled "Lanthannitridoborate(nitride)s" in the group of Prof. H.-Jürgen Meyer at the Institute of Inorganic Chemistry in Tübingen.

H.-Jürgen Meyer, born 1958 in Braunschweig, received his doctorate in 1987 at the Technical University of Berlin with Professor Joachim Pickardt. In the following two years he worked on metal-rich halides of Lanthanide elements at the Ames Laboratory (Ames, Iowa) with Professor John D. Corbett and on band-structure calculations at the Baker Laboratory of the Cornell University (Ithaca, New York) with Professor Roald Hoffmann. In 1989 he moved as a DFG scholarship holder to the University of Hannover, where he completed his habilitation in 1993. As a Heisenberg fellow he was offered professorships at the Universities of Bonn and Tübingen in 1996 and accepted the position in Tübingen. His research interests include syntheses, reactivities, structures, and electronic properties of solids. Present research topics are metal-rich halides, oxocuprates, and metal-C-B-N compounds.

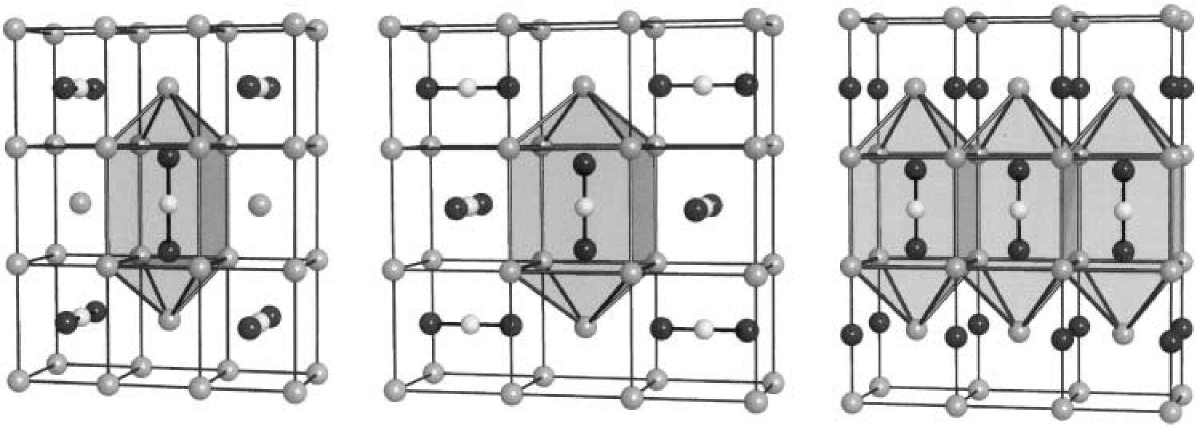


Figure 2. Sections from the structures of α-Li_3BN_2 (left), $E_3(BN_2)_2$ with E = Ca, Sr, Ba, Eu (center), and $Ca_3(BN_2)_2$ (right).

Some of these dinitridoborate compounds have shown their potential as reagents in chemical reactions. Thus $Ca_3(BN_2)_2$ and $Mg_3(BN_2)N$ are used as flux catalysts for conversions of h-BN into its cubic modification.[4, 5] Li_3BN_2, as shown later, has proven to be worthwhile for the synthesis of nitridoborates of the lanthanides, particularly of lanthanum. Our newest experiments point out that nitridoborates and their derivatives (Li_2CN_2, Ca_3Cl_2CBN) can be considered as suitable starting materials for the synthesis of nonmetallic BN, CN, and CBN materials.[25]

1.3 Nitridoborate Compounds of Lanthanides

Nitridoborate compounds contain anionic BN_x units with terminal N atoms. Until recently, nitridoborate compounds of the lanthanides were examined only selectively. In this process, the compounds $Ln_3B_2N_4$ (Ln = La, Ce, Pr, Nd) were characterized by powder neutron diffraction.[26] For $LnBN_2$ (Ln = Pr, Nd, Sm, Gd) only $PrBN_2$ has been characterized by means of single-crystal X-ray analysis.[27] Compounds of the type $Ln_3B_2N_4$ contain $[B_2N_4]^{8-}$ ions, which are structurally analogous to oxalate ions. The formula type $LnBN_2$ can be written alternatively as $Ln_3B_3N_6$ to take into account the presence of cyclic $[B_3N_6]^{9-}$ ions. Based on a single-crystal X-ray analysis the structure of the nitridoborate nitride $Ce_{15}B_8N_{25}$[28] was determined which (in agreement with the structure of $Ce_{15}(BN_3)_8N$) is constructed from $[BN_3]^{6-}$ and N^{3-} ions. To balance all the anionic charges tetravalent cerium must be present. For the isotypic compounds $Ln_{15}B_8N_{25}$ with Ln = La and Pr substitutions with oxide ions in accordance with $Ln_{15}B_8N_{25-x}O_x$ were taken into consideration.[29] Beyond the above mentioned compounds no other nitridoborates of the lanthanide elements were described until 1999.

Syntheses of nitridoborate compounds were straight forward from mixtures of lanthanide powders, their nitrides, and (h-)BN at high temperatures (>1400 °C). In this way the preparations always contained a mixture of reaction products as well as residual starting materials; this is why the B and N content of a preparation is not exactly controllable by this method.

2. Preparative Routes

2.1 Reactions at High Temperatures (>1400 °C)

$La_3B_2N_4$ is produced from reactions of lanthanum powder, lanthanum nitride, and h-BN by induction heating or by arc-melting. In these reactions the starting materials were pressed to a pellet in the molar ratio 1:2:2 and then melted under Ar for approximately half a minute. A typical X-ray powder pattern of the reaction product shows lines from $La_3B_2N_4$, LaB_4, and h-BN. Single crystals of $La_3B_2N_4$ with edges of up to 1 mm can be grown by a subsequent annealing in a sealed tantalum ampoule. With Ce, Pr, and Nd isotypical compounds can also be produced in crystalline form.

2.2 Reactions with $CaCl_2$ as a Flux

A series of interesting compounds in the system alkaline-earth-metal–(B, C, N) have been crystallized from a $CaCl_2$ flux, which was however, often incorporated into the reaction products.[30–32] Dry $CaCl_2$[33] has also been successfully used as a reactive agent for syntheses of several lanthanum nitridoborate compounds. Single-crystalline samples of $La_3B_2N_4$, $La_5B_4N_9$,[34] $La_3B_3N_6$,[35] and $La_5B_2N_6$[36] were obtained from reactions of suitable mixtures of La, LaN, and h-BN in a $CaCl_2$ flux at 1250 °C. Reactions were performed using clean tantalum ampoules as reaction containers which were filled under Ar with the respective reaction mixture (and $CaCl_2$ as a flux). Afterwards the tantalum containers were sealed with an arc-welder and finally sealed into evacuated silica tubes (Figure 3). However, after this method, many compounds still can not be obtained as single-phase products. A prominent side product in several reactions was LaB_4. Also the N content of the nitridoborates is not so controllable because of reactions with the tantalum ampoule.

The synthesis of $Pr_3B_3N_6$ was reproduced from $BN_x(NH)_y(NH_2)_z$ and Pr metal at 1250 °C in a NaCl melt.[37]

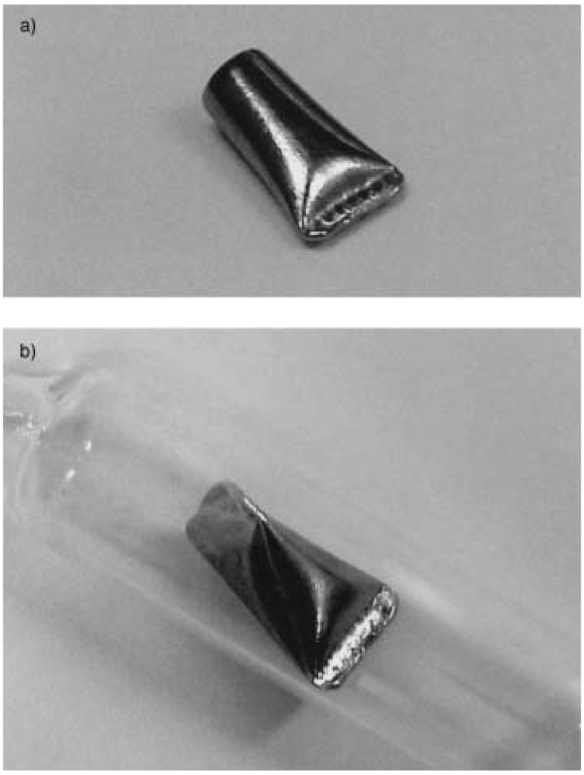


Figure 3. a) tantalum ampoule welded on one side and b) closed tantalum ampoule in an evacuated silica tube.

2.3 Solid-State Metathesis Reactions between $LaCl_3$ and Li_3BN_2

Metathesis reactions between $LaCl_3$ and Li_3BN_2 have turned out to be an efficient method for the preparation of nitridoborates of lanthanum.[38] The Li_3BN_2, required as starting material is produced from a 1:1 mixture of Li_3N and BN in a tantalum ampoule (at 750 °C) or by means of a microwave synthesis in a silica ampoule. Metathesis reactions [Eq. (1)] take place at much lower temperatures than the aforementioned direct syntheses. As can be seen from differential thermal analyses (DTA) the metathesis takes place below 600 °C (Figure 4).

$$3\,LaCl_3 + 3\,Li_3BN_2 \rightarrow La_3B_3N_6 + 9\,LiCl \qquad (1)$$

For the preparation of nitride-rich compounds the N content can be adjusted in the synthesis with Li_3N [Eq. (2)].

$$6\,LaCl_3 + 4\,Li_3BN_2 + 2\,Li_3N \rightarrow La_6B_4N_{10} + 18\,LiCl \qquad (2)$$

2.4 Reductive Solid-State Metathesis Reactions

The preparation of metal-rich nitridoborate(nitride) compounds $Ln_{3+x}(B_2N_4)N_x$ with $x = 0$, 1, 2 of Ln = La, Ce was performed by metallothermic reduction reactions. $La_3B_2N_4$ can be synthesized from a reaction of $LaCl_3$, Li_3BN_2, and La powder in a 3:2:1 molar mixture. However, the use of lithium as reducing agent has turned out to be more efficient in corresponding reactions [Eq. (3)].

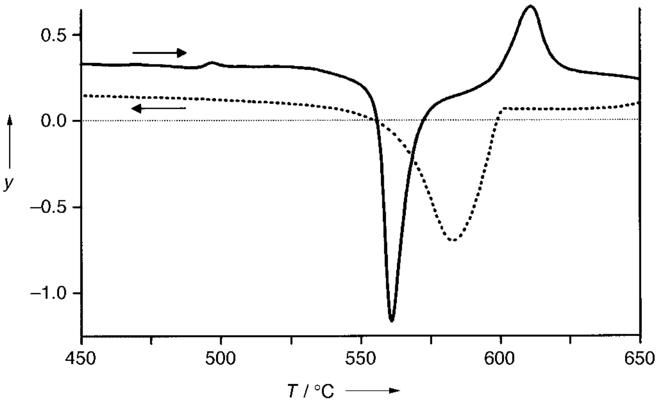


Figure 4. DTA curve (y in μV mg^{-1}) for the reaction in Equation (1) with heating and cooling curve (5 K min^{-1}). The strong exothermic reaction begins at approximately 560 °C. The endothermic effect above 600 °C with heating and the exothermic effect below 600 °C with cooling mark the melting and solidifying of LiCl (m.p. 614 °C).

$$3\,LaCl_3 + 2\,Li_3BN_2 + 3\,Li \rightarrow La_3B_2N_4 + 9\,LiCl \qquad (3)$$

Apart from using lithium as reducing agent for the compositions $La_4B_2N_5$[39] and $La_5B_2N_6$ the nitrogen content can be adjusted by using Li_3N [Eq. (4) and (5)]. After LiCl is removed from the raw products with dry THF, black crystal powders remain as reaction products.

$$4\,LaCl_3 + 2\,Li_3BN_2 + Li_3N + 3\,Li \rightarrow La_4B_2N_5 + 12\,LiCl \qquad (4)$$

$$5\,LaCl_3 + 2\,Li_3BN_2 + 2\,Li_3N + 3\,Li \rightarrow La_5B_2N_6 + 15\,LiCl \qquad (5)$$

During the past few years single crystals of nitridoborate compounds could be grown and pure bulk samples were obtained particularly from applications of solid-state metathesis reactions with Li_3BN_2 and suitable variations of the reaction conditions. However, the development of a universal synthesis route for the preparation of nitridoborate compounds is still in progress.

3. Nitridoborate Ions

Nitridoborate compounds contain BN_x units in which boron tends to the have the coordination number three, as in the structure of hexagonal boron nitride. During the reaction of h-BN with metal nitride compounds (metal = Ln, alkaline, alkaline-earth metal) the BN layers collapse, and nitridoborate ions are formed. The ions $[BN]^{n-}$, $[BN_3]^{6-}$, and $[B_3N_6]^{9-}$ can be considered as charged, integral constituents of the h-BN structure (Figure 5).

Following another route the nitridoborate ions $[BN]^{n-}$, $[B_2N_4]^{8-}$, $[B_3N_6]^{9-}$, and $[BN_3]^{6-}$ can be assembled by solid-state metathesis reactions from $LnCl_3$ with the dinitridoborates Li_3BN_2 or $Ca_3(BN_2)_2$. The structures of nitridoborate ions are closely related to those of known molecules or anions. With CO, CO_2, $[C_2O_4]^{2-}$, and $[CO_3]^{2-}$ the chemistry of the carbon oxides does not have the hypothetical trimer of carbon

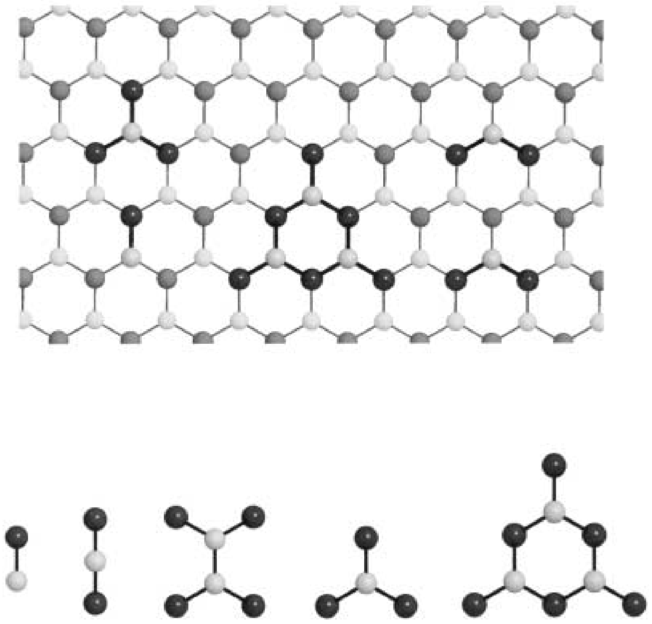
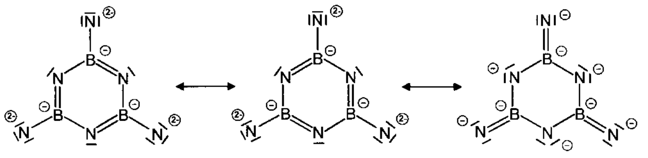


Figure 5. A layer of the h-BN structure with highlighted structure fragments and the nitridoborate ions $[BN]^{n-}$, $[BN_2]^{3-}$, $[B_2N_4]^{8-}$, $[BN_3]^{6-}$, and $[B_3N_6]^{9-}$.

dioxide C_3O_6 which is known for nitridoborates as $[B_3N_6]^{9-}$, for oxoborates as $[B_3O_6]^{3-}$,[40] and for thioborates as $[B_3S_6]^{3-}$.[41] Relationships to these ions (and molecules) as well as the validity of the octet rule characterize the electronic conditions and finally the charges of nitridoborate ions. For the most highly charged ion $[B_3N_6]^{9-}$ some resonance structures are shown in Scheme 1.

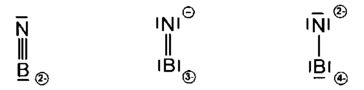


Scheme 1. Selected resonance structures for $[B_3N_6]^{9-}$ with D_{3h} symmetry.

Averaged B–N separations were determined to be 148 pm in $[B_3N_6]^{9-}$, 145 pm in h-BN,[42] and 143 pm in solid borazine ($H_6B_3N_3$).[43] The benzene analogue $H_6B_3N_3$ exhibits, like benzene, six electrons in π states. However, the difference in electronegativity between B and N allows only limited delocalization of the six electrons in the π states. The nine p_z orbitals of the $[B_3N_6]^{9-}$ ion combine to form three bonding π (occupied) combinations, as in borazine, three nonbonding π (occupied) combinations which can be regarded as lone electron pairs of the N atoms, and three antibonding π (empty) combinations.[35]

The chemistry of these highly charged nitridoborate ions in solutions has not been explored to date. This is why the existence of the corresponding nitridoboric acids is in question. Up to now the *ortho*-nitridoboric acid (H_6BN_3), the *meta*-nitridoboric acid (H_3BN_2) and its cyclic trimer ($H_9B_3N_6$) are unknown.

A peculiarity under the nitridoborate(nitride) compounds are metal-rich compounds with B_2N_4 and BN units. Compounds of the formula type $Ln_3B_2N_4$ (Ln = La, Ce, Pr, Nd) contain $[B_2N_4]^{8-}$ ions, isoelectronic to $[C_2O_4]^{2-}$ ions, with B–B separations of approximately 180 pm. The $[BN]^{n-}$ ion may be considered as an intermediate between CO and $[C_2]^{n-}$. Like $[C_2]^{n-}$, $[BN]^{n-}$ can accept different charges depending on the electronic conditions in the respective compound (Scheme 2). Therefore, different bonding conditions with clearly varying bond lengths are expected for B–N bonds in $[BN]^{n-}$ ions.



Scheme 2. Proposed electronic configurations for $[BN]^{2-}$, $[BN]^{4-}$, and $[BN]^{6-}$ ions.

To date, a tetrahedral $[BN_4]^{9-}$ ion with coordination number 4 at the boron atom, as in the cubic BN structure, is unknown for nitridoborate compounds. Among the oxoborates BO_4 tetrahedra are known with mean B–O separation of 148 pm. BO_4 tetrahedra in the structure of the luminescence material EuB_4O_7[44] are constituents of a three-dimensional network.

4. Structure Principles for Nitridoborate Compounds

In solid-state structures, nitridoborate ions form unique regular arrangements. Three structure principles are evident, which basically allow crystal structures of new or hypothetical compounds to be accurately predicted.

- Nitridoborate ions are surrounded in a characteristic way by metal atoms. Terminal N atoms are capped by square-pyramidal arrangements of metal atoms, and the boron atom is surrounded preferably by a trigonal-prismatic array of metal atoms. The nitride ions of nitridoborate nitrides occupy octahedral holes (Figure 6).
- Nitridoborate ions have the tendency to arrange in layers so that layers with the successions $\cdots B \cdots B \cdots$ or $\cdots B \cdots N \cdots$ occur. With compounds containing BN_3 and B_2N_4 units one finds $\cdots B \cdots B \cdots$ stacks. The linear units BN and BN_2 form rod packings.
- Nitridoborate ions can be combined in structures with other nitridoborate ions and with N^{3-} ions in a building-block manner.

From systematic combinations of Ln atoms, nitridoborate, and nitride ions a series of compounds may be expected, some of which have been found. Following our classifications, compounds are considered as parent compounds (nitridoborates) and their nitrides (nitridoborate nitrides) as listed in Table 1. For the compositions Ln_2BN_3 and $Ln_{3+x}(B_3N_6)N_x$ ($x = 1, 2$) specified in Table 1 there is no experimental proof to date. Following the general structure principles for nitridoborate compounds, a crystal structure of the hypothetical compound Ln_2BN_3 is proposed in Figure 7. The central feature of the structure draft are BN_3 units which

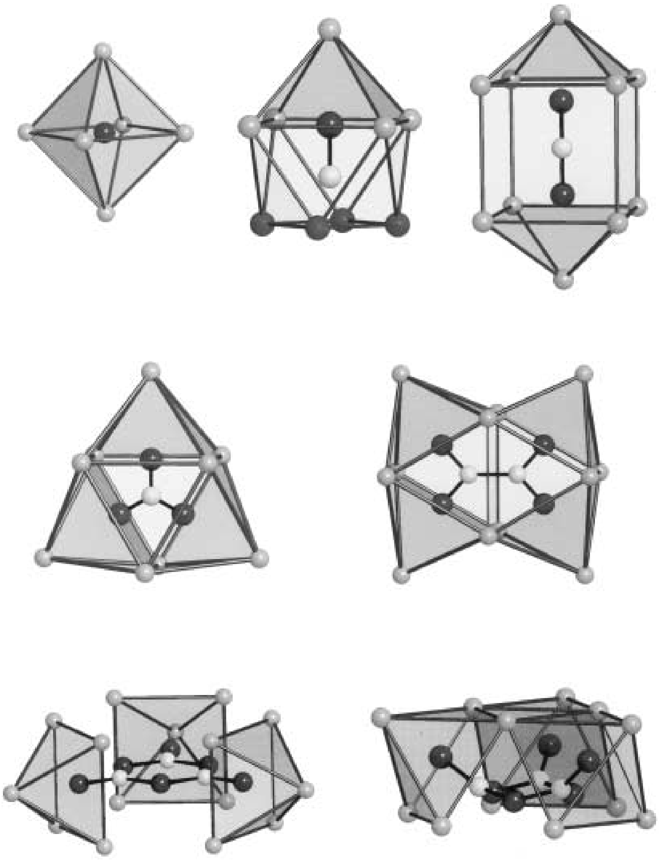


Figure 6. Typical environments of nitride and nitridoborate ions with metal atoms. All N atoms (black) are capped by a (distorted) quadratic-pyramidal formation of metal atoms. For planar and nonplanar B_3N_6 ions two different metal environments occur.

Table 1. Overview of the nitridoborate and nitridoborate nitride compounds of the lanthanides.

Nitridoborate	Ln	Nitridoborate nitride	x	Ln
$Ln_3(BN_2)_2$	Eu[20]	$Ln_{3+x}(BN_2)_2N_x$[a]	–	–
$Ln_2(BN_3)$[a]	–	$Ln_{2+x}(BN_3)N_x$	1	La[25]
$Ln_3(B_3N_6)$[b]	La, Ce,[35] Pr, Nd, Sm, Gd[27]	$Ln_{3+x}(B_3N_6)N_x$[a]	–	–
$Ln_5(B_3N_6)(BN_3)$	La[34]	$Ln_{5+x}(B_3N_6)(BN_3)N_x$	1	La[45]
$Ln_3(B_2N_4)$	La, Ce, Pr, Nd[34]	$Ln_{3+x}(B_2N_4)N_x$	1, 2	La, Ce[36,39]
LnNi(BN)	La, Ce, Pr[54]	$Ln_{1+x}Ni(BN)N_x$	½	La[50, 51]

[a] Unknown. [b] Different structures for compounds with La, Ce, and with Pr, Nd, Sm, Gd.

are surrounded by metal atoms in trigonal-prismatic formations and which are stacked along their pseudo-threefold axis to give $[Ln_{6/2}(BN_3)]$ columns. In the next construction step the columns must be joined in a way so that the composition Ln_2BN_3 results.

5. Saltlike Nitridoborate Compounds and Their Nitride Derivatives

The number of compounds in the system La-B-N is larger than it was at first expected because different types of nitridoborate ions can coexist in structures side by side (Table 1). Additional combinations with nitride ions are known for nitridoborate nitride compounds. An example of such combinations is the series of the compounds $La_3(B_3N_6)$, $La_5(B_3N_6)(BN_3)$, and $La_6(B_3N_6)(BN_3)N$[45] which all can be described as saltlike compounds with $[B_3N_6]^{9-}$, $[BN_3]^{6-}$, and N^{3-} ions.

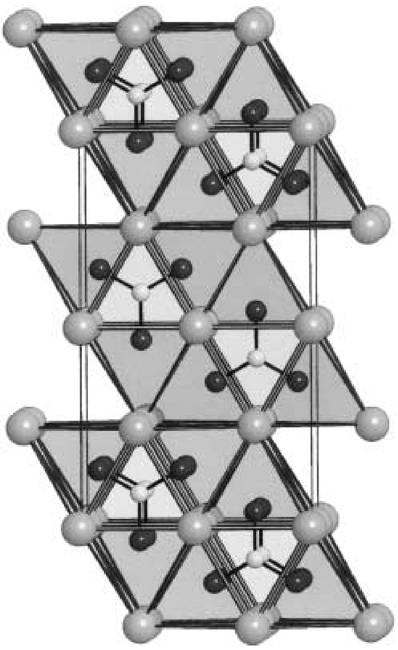


Figure 7. Projection of a structure draft for Ln_2BN_3.

Compounds with the formula $Ln_3(B_3N_6)$ occur with different structures for Ln = La, Ce and for Ln = Pr, Nd, Gd. Both structures contain cyclic B_3N_6 ions however, with a planar conformation for the smaller metal atoms Ln = Pr, Nd, Gd and with a significant deviation from planarity in combination for the larger metal atoms Ln = La and Ce. In the structure of $Pr_3(B_3N_6)$ (space group $R\bar{3}c$) planar B_3N_6 ions are stacked to form columns in staggered formation. The stacking sequence of the B_3N_6 ions in the structure corresponds to a section from the h-BN structure having B$\cdots$N separations of 350.8 pm between B_3N_6 ions in adjacent layers, which is somewhat longer than the 333 pm interlayer distances in the structure of h-BN. In $La_3(B_3N_6)$ ($P\bar{1}$) the B_3N_6 ions are also stacked in columns but in a staggered formation, so that only one ring edge coincides along the stacking direction (Figure 8).

In the structure of $Pr_3(B_3N_6)$, large channel like cavities are occupied by B_3N_6 ions, the exocyclic N atoms of which are fixed in square-pyramidal Pr cavities. The crystals obtained of the formula type $Ln_3(B_3N_6)$ were colorless (the calculated band gap for $La_3(B_3N_6)$ is in the order of 4 eV) or with the characteristic color of the trivalent lanthanoid ion (crystals of $Pr_3(B_3N_6)$ are green) and are marked by their mechanical hardness and chemical stability. Upon heating in air $La_3(B_3N_6)$ reacts above 700 °C to give $LaBO_3$.[46]

In the structure of $Pr_3(B_3N_6)$ all the B–N bonds of the planar B_3N_6 ion are identical within the margins of error (average value 148 pm). Clearly distinguishable B–N bond lengths are, however, found in the nonplanar B_3N_6 ion of $La_3(B_3N_6)$. The B–N bonds determined for exocyclic bonds are between 142 and 147 pm, and those in the ring are

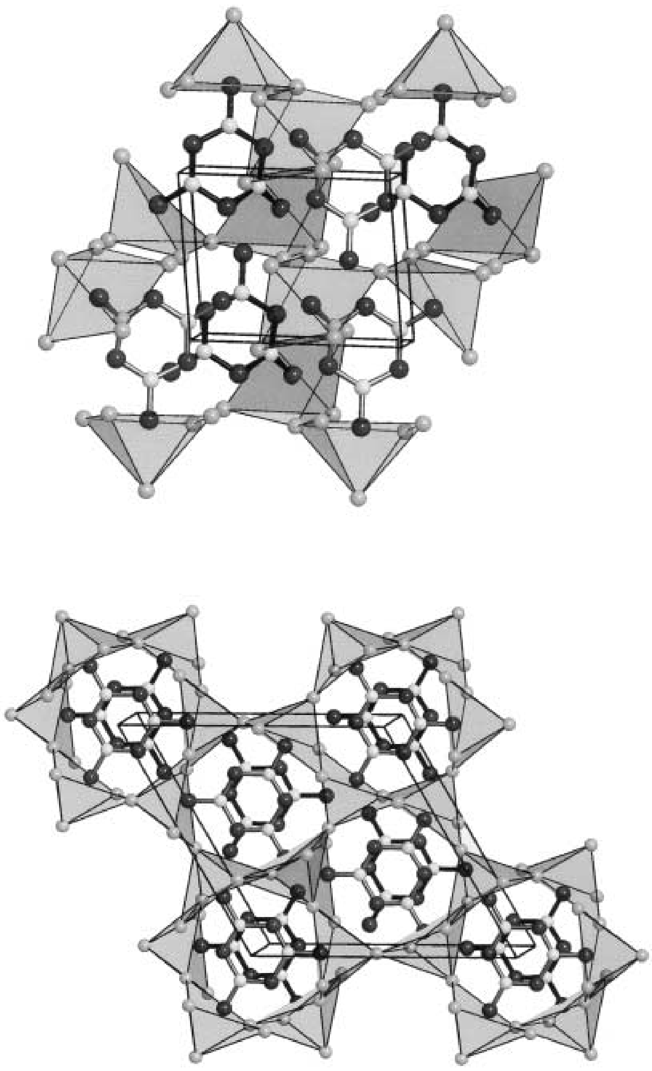


Figure 8. Comparison of the structures of $La_3(B_3N_6)$ (top) and $Pr_3(B_3N_6)$ (bottom).

between 148 and 151 pm. On account of the relatively large errors of the refined light-atom positions the slight differences in the B–N bond lengths may be subjected to a systematic evaluation only with caution. Shorter exocyclic B–N bonds of nonplanar B_3N_6 ions can be interpreted as an increasing localization of the electrons of three π combinations in the direction of the exocyclic bonds (Scheme 1, right). The trend towards shorter B–N bond lengths for exocyclic B–N bonds was also found for B_3N_6 ions in the structures of $La_5B_4N_9 = La_5(B_3N_6)(BN_3)$ and $La_6B_4N_{10} = La_6(B_3N_6)(BN_3)N$. Here the B_3N_6 units are also not planar, but have a chair conformation in which nearly planar BN_3 arrangements at the B atoms are retained. Therefore, a planar conformation is not mandatory for the B_3N_6 unit. Because of the different electronegativity and size of B and N atoms the delocalization of electrons in π states might be limited. One reason for deviations from planarity is evidently a flexibility of the B_3N_6 units to adapt themselves into the prevailing metal matrix of the respective structures.

The B–N bonds of the BN_3 unit in $La_5(B_3N_6)(BN_3)$ and $La_6(B_3N_6)(BN_3)N$ are, at 147–150 pm, not significantly shorter than the mean distances in the B_3N_6 unit. In the structures of $La_5(B_3N_6)(BN_3)$ and $La_6(B_3N_6)(BN_3)N$, the BN_3 units are stacked in columns along the *c* axis (Figure 9). The presence of one additional formula unit LaN (with $y = 0$ and ½) in $La_6(B_3N_6)(BN_3)N$ results in an extension of the *b* axis by approximately 200 pm (Table 2).

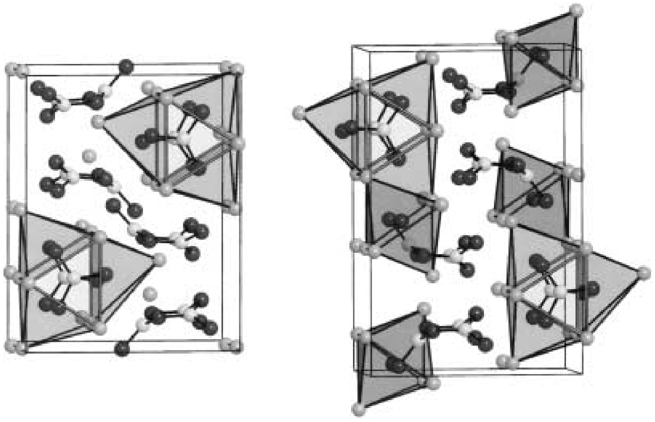


Figure 9. The structures of $La_5(B_3N_6)(BN_3)$ (space group *Pbcm*; left) and $La_6(B_3N_6)(BN_3)N$ (space group $P2_1/c$; right) with four formula units in the unit cell. Projections along the *c* axis.

Table 2. Saltlike lanthanum nitridoborate compounds with B_3N_6 and BN_3 units.

Compound	Space group	Cell constants [pm, °]	*Z*	Cell volume [10^6 pm^3]
$La_3(B_3N_6)$	$P\bar{1}$	$a = 661.3(1)$, $\alpha = 106.06(1)$ $b = 687.01(1)$, $\beta = 90.55(1)$ $c = 779.8(1)$, $\gamma = 115.63(1)$	2	303.5
$La_5(B_3N_6)(BN_3)$	*Pbcm*	$a = 988.25(5)$ $b = 1263.48(7)$ $c = 770.33(4)$	4	961.9
$La_6(B_3N_6)(BN_3)N$	$P2_1/c$	$a = 971.89(6)$ $b = 1479.41(9)$, $\beta = 90.005(9)$ $c = 762.32(4)$	4	1096.1
$La_3(BN_3)N$	[a]	$a = 1263.4(3)$ $b = 1096.6(2)$ $c = 366.53(7)$	4	507.8
$La_6(BN_3)O_6$	*Cmcm*	$a = 366.88(3)$ $b = 2509.2(3)$ $c = 1101.1(1)$	4	1013.7

[a] Space group uncertain.

The nitride ion in $La_6(B_3N_6)(BN_3)N$ occupies a distorted octahedral hole with four shorter (256–266 pm) and two longer (275 and 288 pm) La–N separations. For the octahedral surroundings of N^{3-} ions in the structure of LaN the La–N separations are approximately 266 pm. The BN_3 unit is surrounded by a total of nine lanthanum atoms in the formation of a tricapped trigonal-prism. In the crystal structure the prisms share their triangular faces along the *c* axis to form columns (Figure 10) and these are linked along the *b* axis over nitrogen-centered octahedra. In both structures the stacking of the BN_3 is almost ecliptic.

Although colorless crystals are to be expected in accordance with saltlike charge assignments for $(La^{3+})_5(B_3N_6^{9-})(BN_3^{6-})$ and $(La^{3+})_6(B_3N_6^{9-})(BN_3^{6-})(N^{3-})$ black crystals were

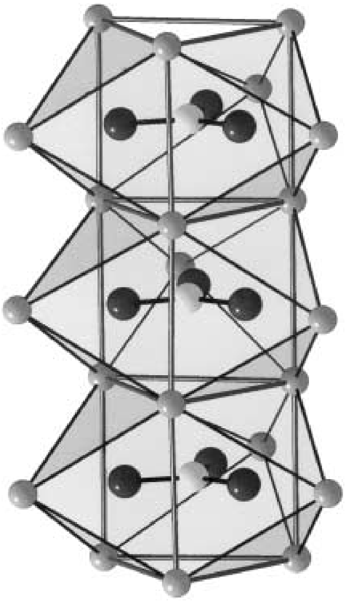


Figure 10. Column of stacked BN_3 units with tricapped trigonal formations of lanthanum atoms (gray) from the structure of $La_6(B_3N_6)(BN_3)N$.

observed as for LaN. Apart from the possibility of crystal defects, a nitride deficiency, which arises also with lanthanide nitrides, could be responsible for this observation.

The typical arrangement of trinitridoborate ions is also evident in the crystal structure of $La_3(BN_3)N$[25] (Figure 11). The BN_3 unit with B–N bonds of approximately 149 pm is located in the center of a tricapped trigonal-prism of lanthanum atoms. The BN_3 centered prisms are stacked to $[La_{6/2}(BN_3)]$ columns through shared triangular faces. Lanthanum atoms in one prism column cap N atoms of the BN_3 units in neighboring columns and at the same time form by their arrangement octahedral cavities for the nitride ions in $La_3(BN_3)N$.

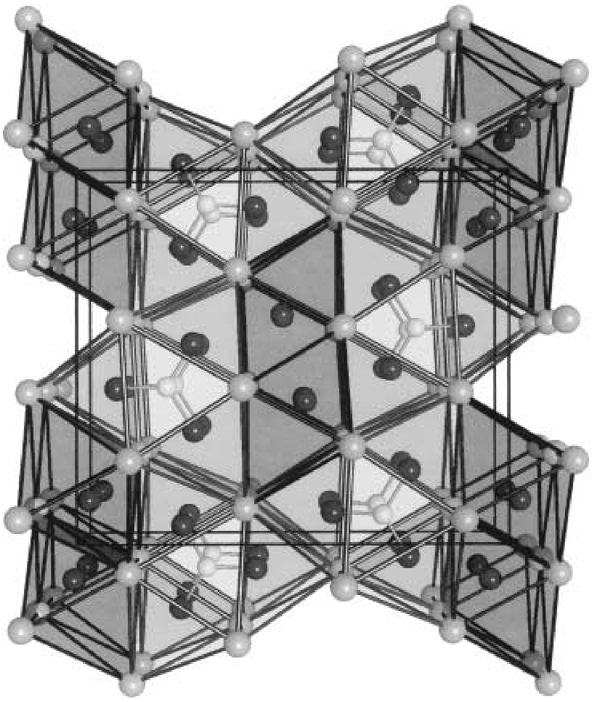


Figure 11. Projection of the crystal structure of $La_3(BN_3)N$ along the *c* axis.

To date the compounds $Ln_{15}(BN_3)_8N$[28, 29] with Ln = La, Ce, and Pr are the only nitridoborates that do not follow the typical structure pattern of approximately ecliptic stacked BN_3 units. They crystallize in the same structure type as the thioborate $K_4Ba_{11}(BS_3)_8S$[47] in which K and Ba atoms occupy equivalent positions. With the charges considered for $[BN_3]^{6-}$ and N^{3-} ions the Ln elements would have to have mixed valences which is improbable for Ln = La. Therefore, partial substitution with oxide in accordance with $(Ln^{3+})_{15}(B^{3+})_8(N^{3-})_{19}(O^{2-})_6$ must be considered.

The transition between nitridoborates and oxoborates opens up the possibility of deliberately modifying certain characteristics of these groups of materials. Knowledge of nitrodoborate nitride compounds poses the question, which anions other than nitride could be combined with the nitridoborate ions? Possible candidates are oxide and halide ions. In an attempt to synthesize nitridoborate oxides, LaOCl is used as an oxygen source. The structure of $La_6(BN_3)O_6$[48] fits nicely into the structure principles typical for nitridoborates. The trinitridoborate ions are surrounded by tricapped trigonal-prismatic arrangements $[La_6La_3(BN_3)]$ of lanthanum atoms. These are stacked over shared triangle faces to form $[La_{6/2}La_3(BN_3)]$ columns. The arrangement of these columns in the structure of $La_6(BN_3)O_6$ leaves cavities which are occupied with O^{2-} ions (coordination number = 4–6; Figure 12).

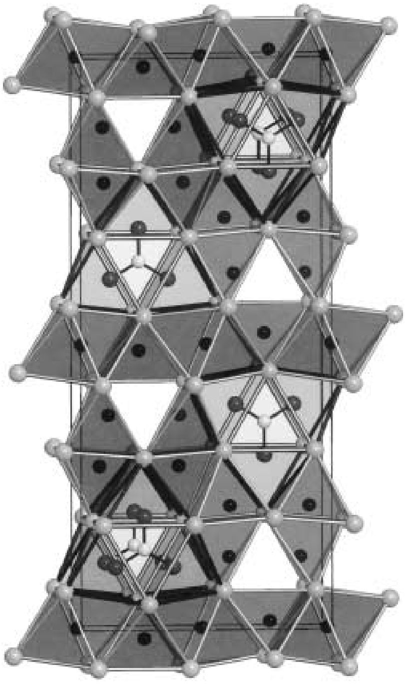


Figure 12. Projection of the crystal structure of $La_6(BN_3)O_6$ along the *a* axis.

6. Metal-Rich Nitridoborate Compounds and their Nitride Derivatives

A peculiarity of Ln nitridoborate compounds is that they can also form metal-rich compounds which is in contrast to, for example, the oxoborates. Metal-rich nitridoborate compounds are known with B_2N_4 and BN units. As in the case for the saltlike nitridoborates, parent compounds arise also with metal-rich nitridoborates from which nitridoborate nitride compounds can be produced by formal addition of metal nitride. Among the parent compounds of metal-rich nitridoborates are $Ln_3(B_2N_4)$ and LnNi(BN). Their nitride derivatives are characterized by the formulations $Ln_{3+x}(B_2N_4)N_x$ with $x = 1$, 2 and $Ln_{1+x}Ni(BN)N_x$ with $x = ½$ (Table 1 and Table 3).

Table 3. Metal-rich nitridoborate compounds with B_2N_4 and BN units.

Compound	Space group	Cell constants [pm, °]	Z	Cell volume [10^6 pm^3]
$La_3(B_2N_4)$	*Immm*	$a = 362.94(3)$, $b = 641.25(6)$ $c = 1079.20(8)$	2	251.2
$La_4(B_2N_4)N$	*C2/m*	$a = 1260.4(1)$ $b = 366.15(3)$, $\beta = 129.727(6)$ $c = 919.8(1)$	2	326.4
$La_5(B_2N_4)N_2$	*C2/m*	$a = 1255.2(1)$ $b = 367.67(4)$, $\beta = 105.967(2)$ $c = 905.76(9)$	2	401.8
LaNi(BN)	*P4/nmm*	$a = 371.96(3)$, $c = 758.23(9)$	2	104.9
CeNi(BN)	*P4/nmm*	$a = 358.45(4)$, $c = 751.4(1)$	2	96.5
PrNi(BN)	*P4/nmm*	$a = 363.21(8)$, $c = 761.7(2)$	2	100.5
CaNi(BN)	*P4/nmm*	$a = 353.38(1)$, $c = 763.76(1)$	2	95.4
CaPd(BN)	*P4/nmm*	$a = 377.38(1)$, $c = 760.95(4)$	2	108.4
$La_3Ni_2(BN)_2N$	*I4/mmm*	$a = 372.51(1)$, $c = 2051.72(4)$	2	284.7

6.1 Compounds with the B_2N_4 Ion

Parent compounds of the type $Ln_3(B_2N_4)$ with Ln = La, Ce, Pr, Nd contain the $[B_2N_4]^{8-}$ ion which is isoelectronic to the oxalate ion. Nitridoborate ions in these structures are in a characteristic metal environment. The boron atoms are integrated into planar B_2N_4 units, and the surrounding trigonal metal prisms combine in pairs to a rhombic prism. The B–B bond lengths are 176–182 pm, and the B–N bonds are at 149–150 pm somewhat longer than the corresponding distances in the h-BN (145 pm). Each of four nitrogen atoms is capped by a square-pyramidal formation of metal atoms. Thus, each N atom of the B_2N_4 unit has a distorted octahedral environment if the neighboring B atom is considered.

In the structures the $[Ln_8(B_2N_4)]$ building blocks with the rhombic-prismatic formation of their Ln atoms are stacked over shared faces to yield $[Ln_{8/2}(B_2N_4)]$ columns along the short lattice translation. All the $[Ln_{8/2}(B_2N_4)]$ columns are connected through two shared edges to form layers and arranged in such a manner that Ln atoms of one column always cap N atoms of B_2N_4 units in neighboring columns (Figure 13).

Departing from the parent compounds $Ln_3(B_2N_4)$, nitridoborate nitrides are known in which the nitride ions occupy octahedral holes. These compounds all can be summarized as $Ln_{3+x}(B_2N_4)N_x$ with $x = 0$, 1, 2 (Table 3, Figure 14). In the structures with $x = 1$ and 2, the arrangement of the $[Ln_{8/2}(B_2N_4)]$ columns alternates with one or two (*trans* edge-sharing) octahedron columns $[Ln_{4/2}Ln_2(N)]$. For the compounds $La_{3+x}(B_2N_4)N_x$ a step by step increase of the cell volume per formula unit of around 38×10^6 pm^3 is registered when going from $x = 0$ to 1 to 2. This increase corresponds to the cell volume of LaN (approximately 37×10^6 pm^3).

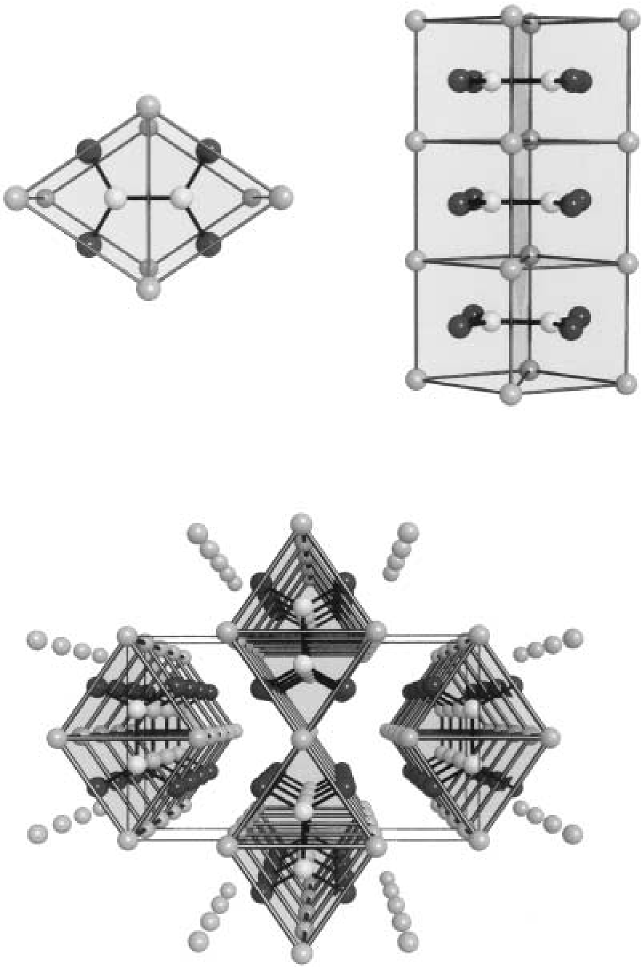


Figure 13. $[Ln_8(B_2N_4)]$ building unit, $[Ln_{8/2}(B_2N_4)]$ column, and projection of the structure of $Ln_3(B_2N_4)$ along the short lattice translation.

These compounds $Ln_{3+x}(B_2N_4)N_x(e^-)$ are unique within the series of lanthanoid nitridoborates, because they possess one surplus electron per formula unit, in the metal 5d bands. The density of states (DOS) calculated for $La_3(B_2N_4)$ and the B–B overlap population resulted in B–B bonding states between the broad anionic valence band and the partially occupied conduction band from (La)5d states (Figure 15). Magnetic measurements of $La_3(B_2N_4)$ samples showed temperature-independent paramagnetic (TIP) behavior.[34]

6.2 Compounds with the BN Ion

To date the mononitridoborate or boronitride ion is known only from quaternary compounds. A relationship which exists between graphite and h-BN could also be considered for compounds with BN and C_2 units. However, the solid-state reactions between Ca and BN (1:1) does not produce Ca(BN), the analogue of CaC_2,[49] but $Ca_3(BN_2)_2$ and CaB_6.

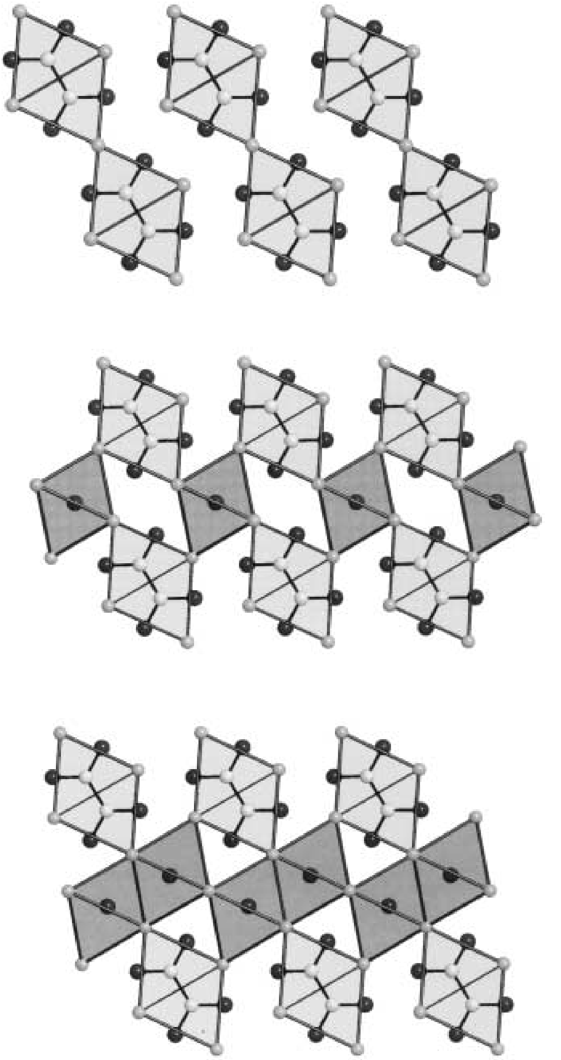


Figure 14. Comparative projections of the crystal structures of $Ln_{3+x}(B_2N_4)N_x$ with $x=0$ (top), 1 (middle), 2 (bottom) along their short lattice translations. The constituent structure fragments $[Ln_8(B_2N_4)]$ and $[Ln_6(N)]$ are highlighted.

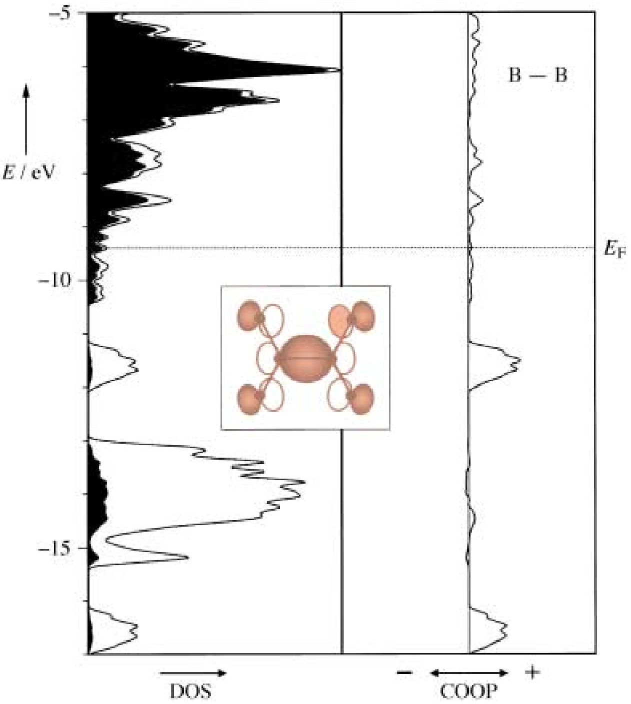


Figure 15. Calculated density of states (DOS) of $La_3(B_2N_4)$ (contribution of lanthanum states marked in black) and B–B crystal orbital overlap population (COOP). The inset shows a molecular orbital (MO) of one bonding B–B combination. The Fermi level (E_F) is marked with a dotted line.

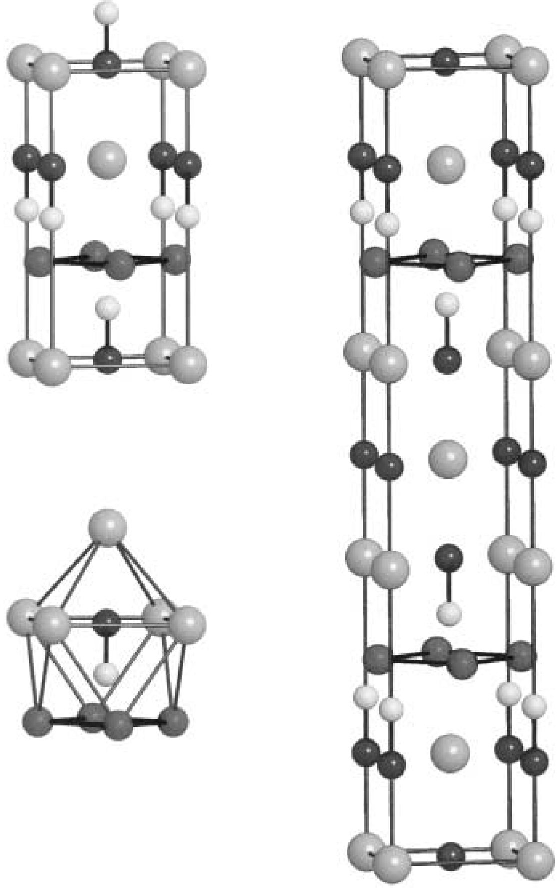


Figure 16. Coordination of the BN unit (bottom left), and structures of LaNi(BN) (top left), and $La_3Ni_2B_2N_3$ (right).

During the years 1994/95 LaNi(BN) and the superconductive compound $La_3Ni_2(BN)_2N$ ($T_c = 12$ K) were prepared with an electric arc from mixtures of La, LaN, Ni, and B.[50] Neutron powder-diffraction analyses for $La_3Ni_2(BN)_2N_{1-z}$ revealed a nitrogen deficiency of $z = 0.09$ and a B–N bond of 144 pm.[51] For LaNi(BN) only electron-microscope data are available, which indicate an unusually long B–N bond of 202(18) pm. For the isostructural compound LuNi(BC) B–C bonds of 152 pm were reported.[52] In the meantime, nitridoborate compounds of the formula type LnM(BN) are known for Ln = Ca,[53] La, Ce, and Pr[54] with M = Ni and Pd (Table 3). In the CaNi(BN) structure the B–N bond length is 138 pm. In comparison with the unknown derivative Ca(BN) of the CaC_2 type the LnNi(BN) structure (Figure 16, left) offers different chemical environments for B and N atoms. Boron atoms (of the BN units) are oriented towards the layer of nickel atoms and cap the face centers of the square-planar formations of nickel atoms from both sides, so that each nickel atom is surrounded tetrahedrally by boron atoms. This characteristic arrangement is observed in the compounds LnNi(BN), $La_3Ni_2(BN)_2N$, and $LnNi_2(B_2C)$ (Figure 16 and 22).

The compounds LnNi(BN) with Ln = La, Ce, Pr have metallic properties and show temperature-independent paramagnetism (TIP) in the temperature range $20 \leq T \leq 300$ K.[54] For CeNi(BN) a magnetic ordering (Figure 17) with a weak hysteresis below 20 K is observed. PrNi(BN) shows additional temperature-dependent paramagnetic portions.

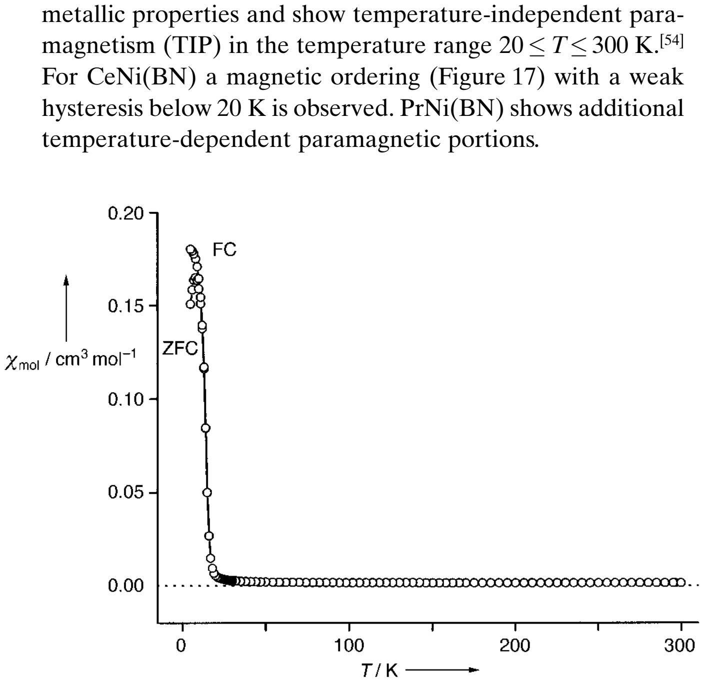


Figure 17. Magnetic ordering of CeNi(BN) (500 G). FC = field cooling, ZFC = zero-field cooling.

The structure of $La_3Ni_2(BN)_2N$ contains additional LaN layers compared with that of LaNi(BN). Our attempts to reproduce the synthesis from the elements and BN resulted in impure products with transition temperatures of 12 K. Only the application of a metathesis reaction based on Li_3BN_2 and $LaCl_3$ resulted in X-ray-pure products[38] on which transition temperatures of 14 K were measured (Figure 18).[54]

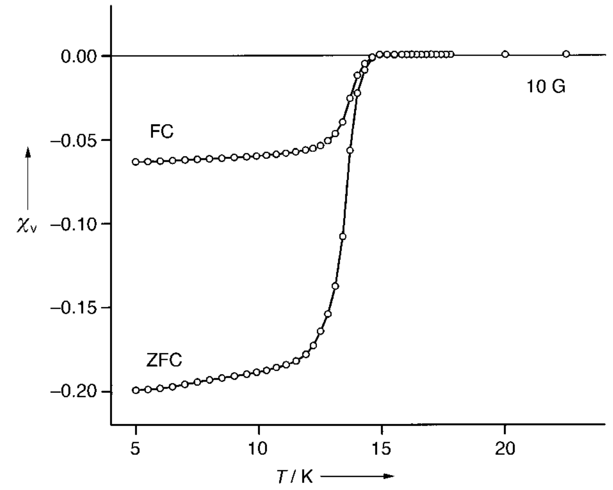


Figure 18. FC and ZFC susceptibilities of $La_3Ni_2(BN)_2N$ (10 G).

Clearly there are different bond lengths and charges to be considered for BN anions in compounds CaNi(BN), LaNi(BN), and $La_3Ni_2(BN)_2N$. Similar situations can be found for dicarbide compounds. The bond lengths are here about 120 pm for $[C_2]^{2-}$ in CaC_2, 128 pm for "$[C_2]^{3-}$" in LaC_2,[55] 135 pm for "$[C_2]^{4-}$" in UC_2, and 149 pm for "$[C_2]^{6-}$" in $Rb\{Pr_5(C_2)\}Cl_{10}$.[56] However, only the charge of C_2 in CaC_2 can be considered as being formally correct. For the electrically conductive compounds LaC_2 and UC_2, delocalized electrons are present which can not be assigned clearly either to the metal or to the C_2 unit. The orbital combination of $(C_2)\pi^*$ and (Ln)5d orbitals corresponds to the HOMO in lanthanoid dicarbide compounds and contains antibonding C–C as well as bonding Ln–C and Ln–Ln interactions. This combination expresses the increase of the C–C bond lengths with rising electron numbers if successive occupations of these orbitals by zero (CaC_2), one (LaC_2), and two (UC_2) electrons take place, as well as the delocalization of electrons in lanthanoid dicarbide compounds (Figure 19).

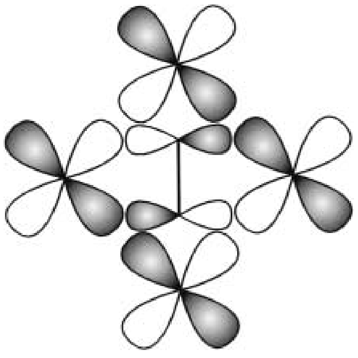


Figure 19. Interaction of one of the two π_g^* orbitals (C_2) with 5d orbitals (Ln) in LnC_2.

6.3 The Electronic Structure of LaNi(BN)

The formula type LnM(BN) is known for CaNi(BN), CaPd(BN), and LnNi(BN) (Ln = La, Ce, Pr). Only for CaNi(BN) is a single-crystal X-ray diffraction determination present, according to which the B–N bond here is 138 pm.[53]

The molecular orbitals of the BN unit show clear differences to those of the C_2 unit[57] although the ordering of the respective energy levels is the same. For a $[C_2]^{2-}$ unit with 10 valence electrons and a bond length of 120 pm the electron configuration is $(2\sigma_g)^2(2\sigma_u)^2(\pi_u)^4(3\sigma_g)^2(\pi_g{}^*)^0$. Contained in it are one strongly bonding $2\sigma_g$ combination and two combinations of lone pairs ($2\sigma_u$ and $3\sigma_g$), of which the $3\sigma_g$ combination represents the HOMO of the $[C_2]^{2-}$ unit. The mixing of the orbitals in the $3\sigma_g$ combination of the BN unit have (because of the nondegenerate B–N interaction) high coefficients located at the boron atom (Figure 20, left). Therefore, the B atom of the BN unit is predetermined to form donor bonds towards soft metal centers through this nonbonding combination—similar to C in CO. At the same time the BN unit can act as an electron acceptor through its π^* orbitals.

The unit cells of the tetragonal LnNi(BN) structures contain two crystallographically identical BN units. The energy bands of the BN partial structure show dispersions (between the special points X-Γ, Γ-M, A-Γ, and Z-R) which are a result of B···B interactions of neighboring BN fragments (Figure 20, middle). If all bonding and nonbonding

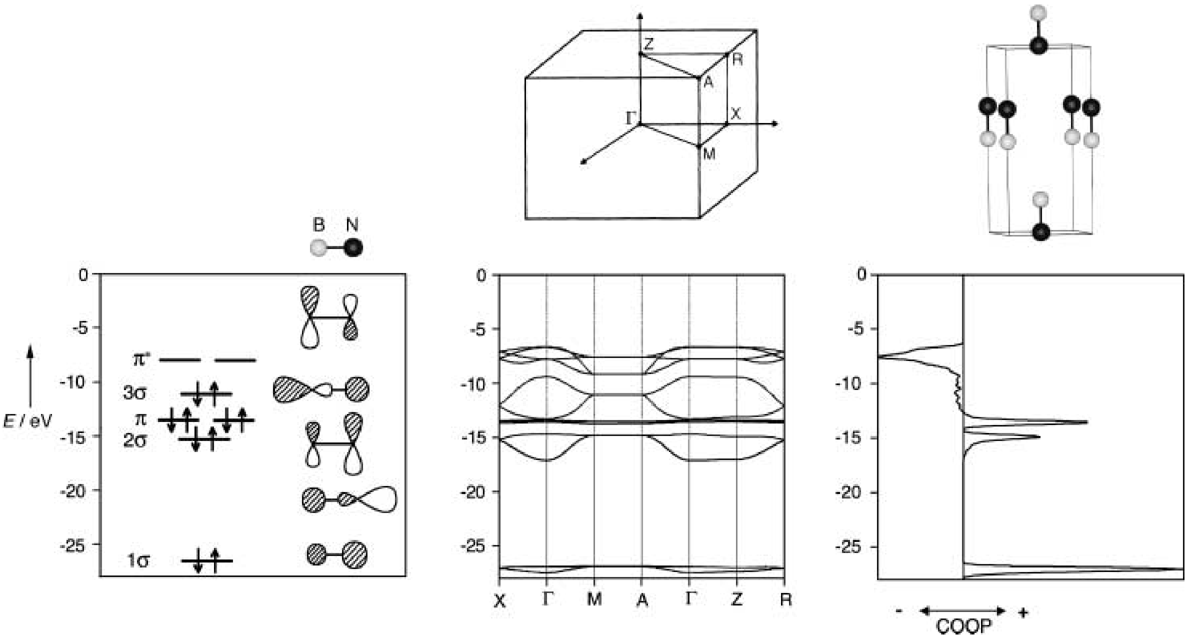


Figure 20. Molecular orbitals of the BN^{2-} unit (left), band structure with corresponding Brillouin zone (center), and B–N overlap population (COOP) of the BN partial structure of LaNi(BN) (right).

B–N states are occupied with electrons, $[BN]^{2-}$ ions can be addressed to the MO as well as to the COOP of the BN partial structure (Figure 20, right). In the projected DOS for LaNi(BN) the contributions of the (La)5d bands and the (Ni)3d bands can be traced as clear peaks at around −7 eV and −14 eV (Figure 21). Thus the (Ni)3d bands are below the Fermi energy in the range of the bonding π levels of BN. The projected B–N overlap populations allows a rough allocation of the electronic states in bonding (1σ, 2σ, π), nonbonding (3σ), and antibonding (π*) with increasing energy. From these the 1σ, 2σ, π, and 3σ corresponding to the energy states for a $[BN]^{2-}$ unit can be considered filled. Because of the bonding and antibonding interactions with metal atoms, the π* energy states are split into two blocks. The position of the Fermi energy for LaNi(BN) indicates that the π* energy states are partially occupied with electrons. From this result a simple charge picture can be derived as $(La^{3+})(Ni^{0})(BN^{3-})$. A similar combination between $(C_2)\pi^*$ and (Ln)5d orbitals is shown in Figure 19 for metal dicarbide compounds. With one electron less per formula unit the antibonding π* orbital for CaNi(BN) is only partially occupied and this should result in a shorter B–N bond. The electronic situation can be given formally as $(Ca^{2+})(Ni^{0})(BN^{2-})$.

In its bonding behavior BN exhibits, through the B atom, σ-donor, but also acceptor capabilities with regard to nickel atoms. Lanthanum has stronger electron-donation properties, since the (La)5d orbitals are higher in energy and transfer charges to the BN unit. Also from this consideration it becomes clear that a charge close to zero is to be assigned to the nickel atoms in these compounds. To date the B–N vibration frequencies of the black LnM((BN) substances are not known.

6.4 Comparisons of Compounds with C_2, BN, and BCB Ions

The structure of $UCoC_2$[58] corresponds topologically to the LnM(BN) structure. This type of structure can be generated

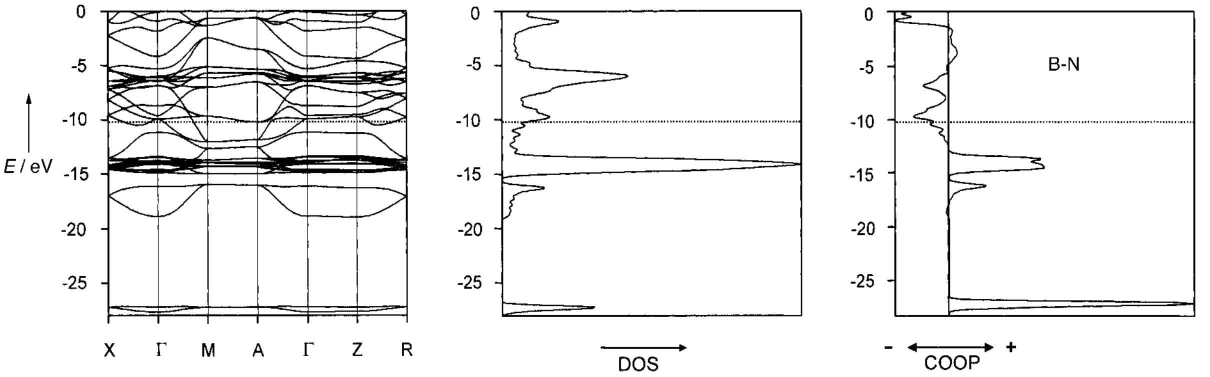


Figure 21. Band structure (left), DOS (center), and B–N overlap population (right) of LaNi(BN). The Fermi level is marked as dotted horizontal line.

by insertion of one atom layer into the tetragonal CaC_2 structure. The $UCoC_2$ type can also be derived from the anti-PbFCl type, as the uranium and cobalt atoms take the positions of chlorine and fluorine and the Pb position is occupied by a C_2 unit. The C–C bond of 148 pm in $UCoC_2$ is in the range accepted as a C–C single bond. If a further atom layer is inserted into the $UCoC_2$ type, the $ThCr_2Si_2$ type[59] results, in which several hundred compounds crystallize (Figure 22).

Special attention was focused on the $LnNi_2(B_2C)$[60] derivative of the $ThCr_2Si_2$ structure type in which the Si_2 unit is replaced by a triatomic B-C-B unit (Figure 22). Compounds with this structure variant exhibit superconductive characteristics with transition temperatures of up to 17 K. Triatomic linear anions with 16 valence electrons such as $[NBN]^{3-}$, $[CCC]^{4-}$, $[CBN]^{4-}$, and $[CBC]^{5-}$ are known from numerous saltlike compounds. Their bond lengths are a good reference system for metal-rich compounds containing these units. An example with a $[BCB]^{6-}$ ion has to date not been reported for saltlike compounds. This situation is not surprising, since, according to a general rule[61] which is supported by theoretical calculations,[62] the more electonegative atom in an $[X=Y=Z]$ trimer with 16 valence electrons has a tendency to occupy a terminal position of the triatomic unit. The superconductive compound $LuNi_2(B_2C)$[63] contains a linear [B-C-B] ion with a B–C bond length of 147 pm. In the linear $[CBC]^{5-}$ ion of $Al_3(C)(BC_2)$[64] the B–C bond lengths is 144 pm, as in the compounds $Ca_9Cl_8(BC_2)_2$[65] and $Ca_5Cl_3(C_2)(BC_2)$[66] (145 and 144 pm) which have slightly bent [C-B-C] units (162 and 164°). In such a linear trimer with 16 valence electrons the HOMO is formed by the nonbonding π_g orbitals.[67] In conformity with the octet rule the full occupation of the nonbonding π_g orbitals would correspond to a $[B=C=B]^{6-}$ ion. Extended Hückel (EH) calculations of the electronic structure of $LuNi_2(B_2C)$ were interpreted in that the π_g orbitals are only partially occupied, and lead to a formal charge description of $(Ln^{3+})(Ni^0)_2(B_2C^{3-})$.[68, 69] The complete occupation of the (Ni)3d bands is also supported by local density approximation (LDA) calculations[70] according to which the (Lu)5d bands (mainly $d_{x^2-y^2}$ orbitals) dip below the Fermi level, and are thus partially occupied and therefore responsible for the mobility of charge carriers.

7. Summary

Nitridoborate compounds of the lanthanides can be produced in different ways: by direct reaction of metal and/or metal nitride together with h-BN and by solid-state metathesis reactions between $LnCl_3$ and Li_3BN_2. The exothermic metathesis reaction between $LnCl_3$ and Li_3BN_2 occurs below 600 °C. Single crystals are formed at higher temperatures from the LiCl flux formed in the reaction. In modified metathesis reactions the N content can be controlled by using Li_3N as a nitride source. The additional use of lithium leads to the synthesis of metal-rich Ln nitridoborate compounds.

Compounds with the anionic units BN, BN_2, B_2N_4, B_3N_6, and BN_3 are known with electropositive (alkaline, alkaline-earth, lanthanide) metals. The B_3N_6 unit occurs both in planar and in nonplanar conformations. Compounds of the type $Ln_3B_3N_6$ stand out for their mechanical hardness. Nitridoborate compounds of the alkaline-earth metals, perhaps also of the Ln metals, can be used for conversions of h-BN into its cubic modification.

Transition metals do not tend to form nitridoborate compounds, because electrons in B–N bonds can have a reducing effect on 3d metal ions. Therefore, Ni^{2+} in $NiCl_2$ is readily reduced by Li_3BN_2 at 300–400 °C to the metal.[38] Transition metals nevertheless can occur in pseudo-ternary nitridoborate or ternary dicarbide compounds. The relationship between C_2 and BN is emphasized by structures of the $UCoC_2$ type and is further supported by the similarities between the carbidometallates Na_2MC_2 (M = Pd, Pt)[71] and “nitridoboratometallates” CaM(BN) (M = Ni, Pd). Also the compounds Na_2MC_2 contain neutral M atoms and twofold negatively charged C_2 ions (C–C bond: 123 pm). Since the charges of BN and C_2 units cannot be assigned precisely for compounds with metallic properties, the distances in the

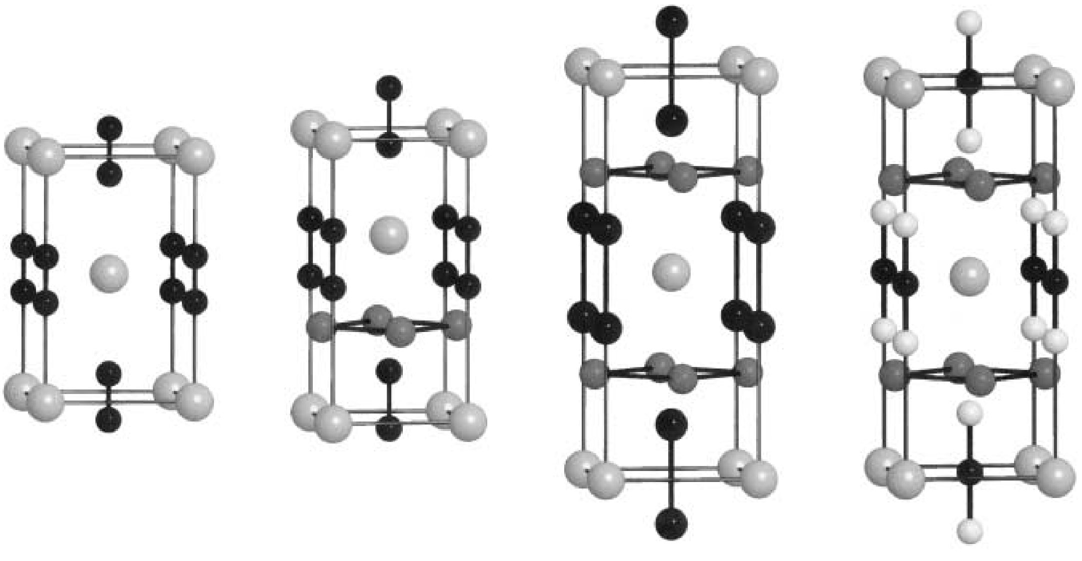


Figure 22. Comparison of the structures of CaC_2, $UCoC_2$, $ThCr_2Si_2$, and $LuNi_2(B_2C)$ (from left to right).

diatomic anions serve—provided they are known accurately—as a probe for their electronic condition. For the normal or superconducting properties $[BN]^{n-}$ ions serve as a charge reservoir which is increasingly emptied in the series $La_3Ni_2(BN)_2N_{1-x}$ ($x = 0.09$), LaNi(BN), CaNi(BN) if one assumes a d^{10} configuration for the nickel centers.

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