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Lanthanide Nitrido Borates with Six-Membered B_3N_6 Rings: $Ln_3B_3N_6$**

Olaf Reckeweg and H.-Jürgen Meyer*

Nitrido borates of the lanthanides contain BN_x units in which boron tends to adopt coordination number three as in the structure of hexagonal boron nitride (α-BN). The coordination number four is only found for boron in the cubic form of boron nitride (β-BN). The coordination number two is reported for a large number of compounds, for example, of the type $A_3(BN_2)_2$ with A = Ca, Sr, or Ba.[1] Under pressure these compounds, together with hexagonal boron nitride, form an eutectic mixture, thus catalyzing the conversion of α-BN into its cubic modification (β-BN).[2] The BN_2^{3-} ions (16 electrons) of the $A_3(BN_2)_2$ structure type are isoelectronic and isostructural to CO_2. The same can be said of BN_3^{6-} (24 electrons)[3] and CO_3^{2-} or $B_2N_4^{8-}$ (34 electrons) and $C_2O_4^{2-}$.

Some nitrido borates of the lanthanides exhibit short metal–metal distances and interesting electric or magnetic properties. For Ln^{3+}, the compounds $Ln_3B_2N_4$ (Ln = La, Ce, Pr, Nd)[4] have one electron per formula unit in the conduction band.[5] These compounds as well as $Ce_3B_3N_6$ have been obtained as black, crystalline substances. Crystals of $La_3B_3N_6$ are colorless and transparent.

The crystal structures of the isostructural title compounds $Ln_3B_3N_6$ (Ln = La or Ce) contain the six-membered B_3N_6 ring with three exocyclic nitrogen atoms. This ring can be regarded as a fragment from a layer of hexagonal boron nitride. The triclinic crystal structures of $Ln_3B_3N_6$ are built up of lanthanide atoms and B_3N_6 rings in a rather complicated way (Figure 1).[6] The B_3N_6 units are centered in layers near $x = 0$ and 1. Two of the three crystallographically different Ln atoms in the structure build puckered layers (near $x = 0.5$) which are alternately capped from above and below by the third Ln atom. This results in a distorted square-pyramidal arrangement of metal atoms. Each of these motifs is occupied by one exocyclic N atom ($5 \times d$(La–N) = 255–265 pm, $5 \times d$(Ce–N) = 252–263 pm) of the B_3N_6 ring. This kind of square-pyramidal arrangement of metal atoms is typical for the coordination environment of terminal N atoms in various nitrido borate ions.[5, 7] The shortest Ln–Ln distances of 355 pm in $La_3B_3N_6$ and of 350 pm in $Ce_3B_3N_6$ are shorter than those in the corresponding metal (the shortest distances here are 375 pm for La and 365 pm for Ce). Short metal–metal distances have also been observed in related compounds $LnBN_2$ of the smaller lanthanides (Ln = Pr, Nd, Sm, Gd), whose structures are based on a different packing order.[7] In these structures the nitrido borate units are piled to form $^1_\infty[B_3N_6]$ columns with the stacking sequence like that of α-BN.

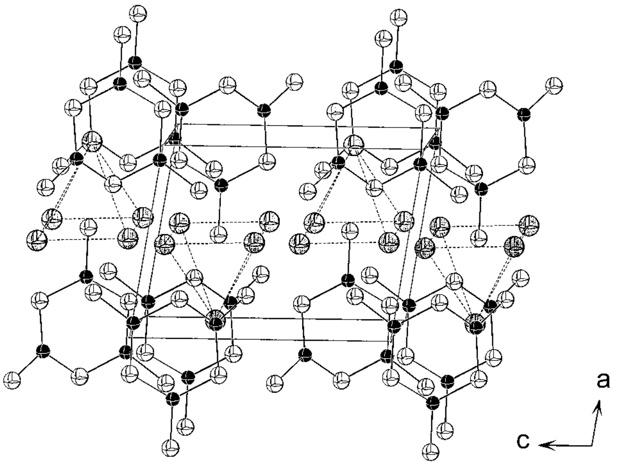

Figure 1. Section of the crystal structure of $Ln_3B_3N_6$ (Ln = La, Ce) with six-membered B_3N_6 rings.

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[*] Prof. Dr. H.-J. Meyer
Institut für Anorganische Chemie
Auf der Morgenstelle 18, D-72076 Tübingen (Germany)
Fax: (+49) 7071-29-5702
E-mail: juergen.meyer@uni-tuebingen.de

Dr. O. Reckeweg
Box 91, Baker Laboratory, Department of Chemistry
Cornell University, Ithaca, NY 14853-1301 (USA)

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As the calculated electronic structure of $La_3B_3N_6$ shows, $Ln_3B_3N_6$ compounds with Ln^{3+} ions should be (transparent) insulators with a band gap on the order of 4 eV (Figure 2).[8] The crystals we have obtained for the lanthanum compound are colorless and transparent, while crystals of the cerium compound appeared black. A possible explanation for this observation might be that the cerium ions do not exist in the configuration Ce^{3+} ([Xe]$4f^1 5d^0$), but in the different state $Ce^{4+}(e^-)$ ([Xe]$4f^0 5d^1$). Following this assumption, the surplus electron would occupy the conduction band. The expected ionic radii (for the coordination number eight) are 118 pm for La^{3+} and 114 pm for Ce^{3+}.[9] The clearly smaller value of 97 pm reported for Ce^{4+} cannot be found in the structure of $Ce_3B_3N_6$. The cerium–nonmetal distances in $Ce_3B_3N_6$ are only 1–5 pm shorter than the lanthanum–nonmetal distances in $La_3B_3N_6$. Instead of the effective ionic radii, the molar volume may be considered as an indicator for the valence state of the metal. The decrease of the molar volume from $LaBN_2$ ($V_m = 30.5\ cm^3 mol^{-1}$) to $CeBN_2$ ($V_m = 29.7\ cm^3 mol^{-1}$) follows the trend of the lanthanide contraction. However, this change is not big enough to justify the assumption of a participation of the [Xe]$4f^0 5d^1$ configuration for the cerium compound.[10] The correct configuration and the charge of cerium in $Ce_3B_3N_6$ will have to be determined with different techniques.[11]

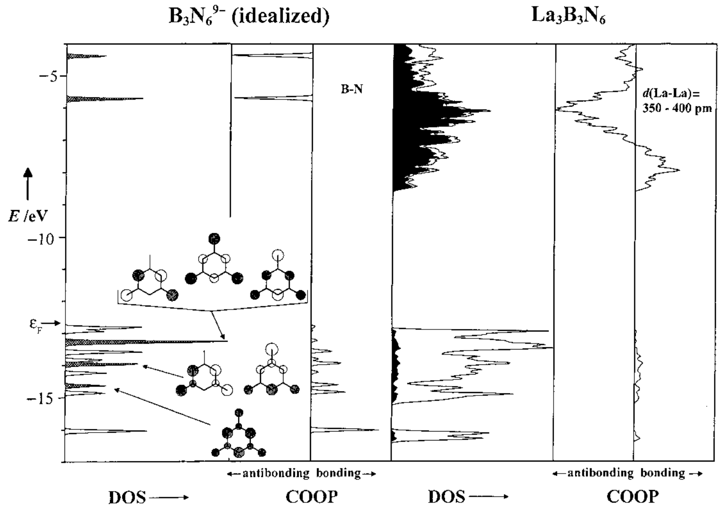

Figure 2. Left: Density of states (DOS) of an idealized $B_3N_6^{9-}$ structure (D_{3h}, d(B–N) = 148 and 145 pm). States having π symmetry are drawn in crosshatch, and some corresponding molecular orbitals exhibiting π symmetry are displayed. Crystal orbital overlap populations (COOP) are projected to show the B–N bonding, nonbonding, and antibonding interactions in the $B_3N_6^{9-}$ unit. Right: Calculated density of states (DOS) of $La_3B_3N_6$ (La contributions to the DOS of $La_3B_3N_6$ are shown in black) and La–La overlap populations (COOP). The Fermi level for $La_3B_3N_6$ is above the bonding B_3N_6 block (at about −12.7 eV).

The deviation of the B_3N_6 rings from their ideal symmetry (D_{3h}) is remarkable (C_s). The B–N distances in the six-membered ring (146–150 pm, av 148 pm) are somewhat longer than those between boron and exocyclic N atoms (144 pm). For comparison the B–N distances in hexagonal BN are about 145 pm, and in borazine ($B_3N_3H_6$)[12] and tris(dimethylamino)borazine ($(NHBNMe_2)_3$)[13] they are about 143 pm. Borazine, like benzene, has six π electrons. Because of the differences in electronegativity and size between boron and nitrogen, there is only a limited delocalization of the six π electrons in borazine. This explains the spontaneous addition reactions with HX or X_2 (X = halide).[14] The $B_3N_6^{9-}$ unit has nine p orbitals that could form π bonds. For these orbitals we found three bonding combinations similar to those in borazine, three nonbonding combinations (these six orbital combinations are shown in Figure 2) and three antibonding combinations.[15] The nonbonding orbitals can be considered lone pairs of the nitrogen atoms. Following group theory their combinations can be viewed as one a and one e state that are close to each other in energy. An expected result of our MO calculations[15] was that the exocyclic nitrogen atoms of an idealized $B_3N_6^{9-}$ ion have a larger negative charge (−2.3) than nitrogen atoms in the six-membered ring (−1.8). The ring conformation or deformation in the solid state not by only governed by the criterion of minimizing the energy of the B_3N_6 unit, but also by the goal to form a close-packed arrangement of B_3N_6 units and Ln atoms. This can be seen, for example, in the structure of $La_5B_4N_9$, where B_3N_6 units adopt a chair conformation, or in the structures of $LnBN_2$ (Ln = Pr, Nd, Sm, Gd), where the B_3N_6 units are nearly planar.[5, 7]

Only one boron atom in the B_3N_6 unit of $Ln_3B_3N_6$ (Ln = La, Ce) is coordinated in a trigonal-planar fashion by nitrogen atoms. The ring distortion in the title compounds is more pronounced than in solid borazine (C_2 symmetry),[12, 16] which has only very little effect on the electronic structure of $La_3B_3N_6$.[8] The occupied energy levels of an idealized $B_3N_6^{9-}$ structure (D_{3h}) can be compared with the calculated density of states for $La_3B_3N_6$. Some of these energy levels split for the real B_3N_6 unit in $La_3B_3N_6$, for example the twofold degenerate σ combination near −16 eV. If the interactions with the Ln atoms are taken into consideration, some of the energy levels are lowered because of Ln–B_3N_6 bonding interactions (Figure 2). The conduction band is dominated by metal states and contains only small contributions from the orbitals of the nonmetal atoms. A formal description of $B_3N_6^{9-}$ ions is supported by the large band gap between the valence band and the conduction band. An analysis of the La–La overlap populations in the structure exhibits bonding states in the conduction band (see COOP in Figure 2, right). Therefore, it seems possible that cerium exists as Ce^{4+} in $Ce_3B_3N_6$ and that the compounds $Ln_3B_3N_6$ could be chemically reduced.

Like borazine, the $Ln_3B_3N_6$ compounds with their B_3N_6 unit may be possible candidates for addition reactions in solution. Another interesting aspect would be the use of $Ln_3B_3N_6$ for the conversion of hexagonal BN into its cubic modification.[2]

Experimental Section

A general approach for synthesizing metal nitrido borates is by direct reaction of metal nitride with α-BN. For this purpose CeN was prepared by the reaction of cerium metal (Strem, 99.9%) under flowing ammonia (at 1027 K, 24 h). LaN was purchased (Alfa, 99%). α-BN (ABCR, 99.8%) was degassed under vacuum conditions before use (at 675 K). $CaCl_2$ was employed as a flux (dried for 4 h at 675 K under flowing HCl). All employed reagents and reaction containers were handled in a glove box under dried argon.

$Ln_3B_3N_6$ was synthesized by the reaction of LnN (Ln = La or Ce) with α-BN at 1500 K in a $CaCl_2$ flux (molar ratio 1:5:1). Arc-welded tantalum ampoules (Plansee) were used as reaction containers. The ampoules were sealed in evacuated silica tubes to shield them from moisture and air. $La_3B_3N_6$ was obtained as colorless, transparent single crystals, and $Ce_3B_3N_6$ as black single crystals with defined faces but irregular shape.

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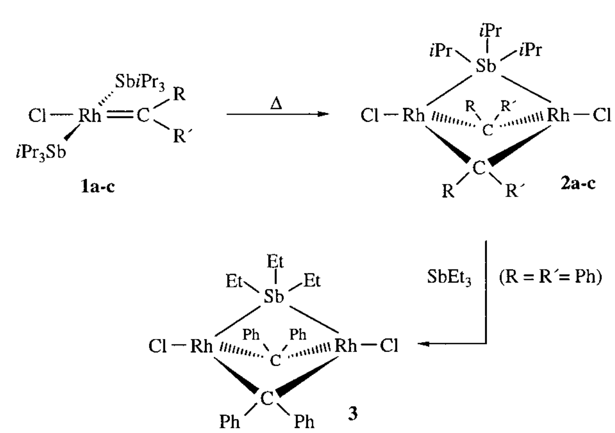
Formation of Novel Dinuclear Mixed-Valence Rhodium Complexes by Intramolecular Migration of a Chelating Ligand**

Ulrich Herber, Birgit Weberndörfer, and
Helmut Werner*

*Dedicated to Professor Nils Wiberg
on the occasion of his 65th birthday*

One of the most surprising results of recent work from our laboratory was that trialkylstibanes can function as bridging ligands in dinuclear transition metal complexes. In the course of investigations concerned with the reactivity of square-planar carbenerhodium(I) compounds **1**, which were obtained from *trans*-[RhCl(C_2H_4)(Sb*i*Pr_3)$_2$] and diazoalkanes RR′CN_2 in excellent yields,[1] we discovered that these compounds are thermally quite labile and react upon heating in benzene at 80 °C by partial elimination of Sb*i*Pr_3 to afford the Rh_2 complexes **2** (Scheme 1).[2] The notable feature is that the coordination geometry around the two metal centers of **2**, which are formally in the oxidation state +I, is distorted tetrahedral and that this geometry is preserved in the reactions with $SbMe_3$ or $SbEt_3$ (formation of **3**).[2] In textbooks and standard references it was generally considered as highly improbable[3] that trialkylstibanes as well as their phosphorus and arsenic counterparts can undergo a bridging coordination mode, and this expectation seemed to be confirmed by numerous studies on the chemistry of ligands of the general type ER_3 (E = P, As, Sb).[4]



Scheme 1. **a**: R = R′ = Ph; **b**: R = R′ = *p*-Tol; **c**: R = Ph, R′ = *p*-Tol).

Following our initial studies on the reactivity of **2** toward CO, CN*t*Bu, SbR_3, P*i*Pr_3 etc.[2, 5] we were interested to know whether the dinuclear structure with the core molecular fragment Rh(μ-Sb*i*Pr_3)(μ-CPh_2)$_2$Rh would be maintained if the axial chloro ligands are replaced by chelating anions. The outcome of this substitution would be of course an increase in

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[*] Prof. Dr. H. Werner, Dipl.-Chem. U. Herber,
Dipl.-Chem. B. Weberndörfer
Institut für Anorganische Chemie der Universität
Am Hubland, D-97074 Würzburg (Germany)
Fax: (+49)931-888-4605
E-mail: helmut.werner@mail.uni-wuerzburg.de

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