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Small Boron Carbon Chains Stabilized in Rare Earth Metallic Frameworks: A Bonding Analysis

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The bonding properties of rare earth metal boron carbide compounds are analyzed by means of extended Hückel tight-binding and *ab initio* calculations. Results indicate that these compounds can be described in first approximation as being built of cumulene-like B_xC_y anionic units interacting with not fully oxidized metallic cations. © 1997 Academic Press

INTRODUCTION

The combination of boron and carbon elements with rare earth metals leads to the formation of ternary materials having interesting physical and structural properties. In these compounds of formula $M_xB_yC_z$, the nonmetal atoms generally form either two-dimensional (2-D) networks, or monodimensional (1-D) zigzag chains, or finite linear units of various length inserted in a metallic matrix. Indeed the dimensionality of the boron–carbon sublattice is related to the averaged valence electron count (VEC) per light atom (B or C). This VEC can be calculated assuming a simple ionic bonding scheme between the boron–carbon network and the metal atoms considered as being fully oxidized M^{n+} (i.e., $n = 3$ generally, or possibly 4 as for Ce, Th, or U for example) in the following way: $\mathrm{VEC} = (nx + 3y + 4z)/(y + z)$. Compounds in which 2-D boron–carbon planar networks alternating with 2-D sheets of metal atoms are present have the lowest values of VEC, between 4.1 and 4.7 (1, 2). The class of materials in which the carbon and boron atoms form branched zigzag 1-D systems embedded in a metallic lattice corresponds to values of VEC around 5 (3). Materials containing finite units of nonmetal atoms encapsulated in metallic channels are more electron-rich, with VEC values spreading over the range 4.9–5.7 (4, 5). Although there is not a clear cut in the VEC variation when going from one class to another one, it shows clearly the relationship between the dimensionality and the electron richness of the boron–carbon network. Formal addition of electrons results in the occupation of antibonding orbitals and consequently leads to some bond breaking inside the boron–carbon sublattice.

Such an empirical description of the bonding in these materials needs of course to be completed with detailed results obtained from quantum mechanical calculations. As part of theoretical studies devoted to the rationalization of the structural arrangement of these rare earth metal boron carbides and related phases (1–5), we analyze here the bonding in the compounds listed in Table 1 containing finite boron–carbon units.

DESCRIPTION OF THE STRUCTURES

In all compounds, the metallic sublattice results from a regular or irregular stacking of two-dimensional (2-D) square nets, giving rise to a three-dimensional (3-D) framework with metal–metal separations comparable to that measured in metallic elements. In some cases, the 2-D square nets can be slightly corrugated. Such an arrangement leads to the formation of small channels of different sizes in which roughly linear B_xC_y units are encapsulated, as exemplified by Sc_2BC_2 which contains C–B–C entities (see Fig. 1).

Figure 2 summarizes the different finite boron–carbon units which have been stabilized in ternary rare earth metal boron carbide compounds. Two-atom (C_2) and/or three-atom (BC_2) chains are found in metal- and carbon-rich compounds such as Sc_2BC_2 (4), $La_5B_2C_6$ (5, 6), and $Gd_5B_2C_5$ (7). Longer chains are observed when the B/C ratio increases such as in $La_{15}B_{14}C_{19}$, which contains 11-membered B_4C_7 and B_5C_6 units, $Ce_{10}B_9C_{12}$, in which are inserted 13-membered B_5C_8 chains (the longest so far observed in these compounds), and 8-membered B_4C_4 chains, and $Ce_5B_4C_5$, which contains 3-membered BC_2, 6-membered B_3C_3, and 8-membered B_4C_4 chains, in addition to

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TABLE 1
Rare Earth Metal Boron Carbide Compounds Containing Finite Boron–Carbon Units

Structural type	VEC[a]	B–C network	B/C	Ref.
$La_{15}B_{14}C_{19}$	4.94	$[B_4C_7][B_5C_6]$	0.74	5, 6
$Ce_{10}B_9C_{12}$ (La, Nd)	5.00	$[B_5C_8][B_4C_4]$	0.75	5, 6
$Ce_5B_4C_5$	5.22	$[B_4C_4][B_3C_3][BC_2][C]$	0.8	5, 6
$La_{10}B_9C_6$	5.40		1.5	7
$U_5B_2C_7$ (Ho)	5.44		0.29	8
$Ce_5B_2C_6$ (La, Gd, Ho)	5.63	$[BC_2][C_2]$	0.33	9
Sc_2BC_2 (Nd)	5.67	$[BC_2]$	0.5	4
$Gd_5B_2C_5$	5.86	$[BC_2][C]$	0.4	7
$Gd_{15}B_4C_{12}$	6.56		0.33	7

single C atoms (5, 6). The B–B, B–C, and C–C bond distances, which vary between 1.57 and 1.68 Å, 1.43 and 1.58 Å, and 1.30 and 1.35 Å, respectively, suggest some double bond character. The associated bond angles vary from 180° to ca. 140° (see Fig. 2).

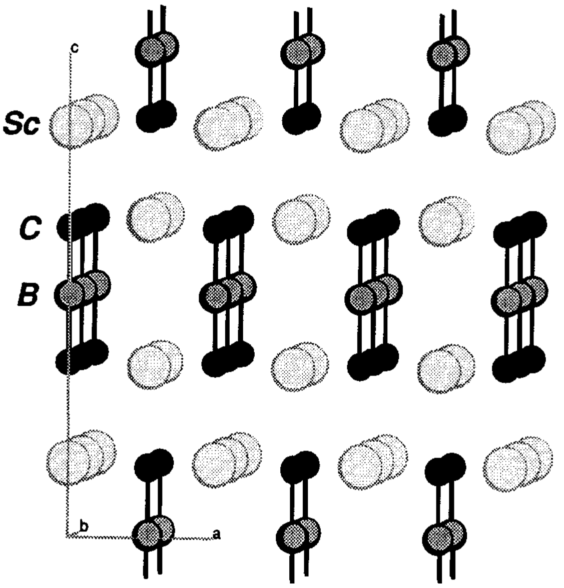

FIG. 1. Structural arrangement in Sc_2BC_2.

BONDING ANALYSIS

The boron–carbon "ligands" can be considered as being cumulene-like molecules complexed by the metallic framework. Previous theoretical studies have shown that an ionic bonding picture between the metallic and the boron–carbon sublattices is often sufficient to explain the structural arrangement encountered in these kinds of material (1–5). The first question which arises then concerns the assignment of formal ionic charges to account for the cumulene-like character of the boron–carbon units. The usual oxidation state for the La and Ce is 3+ (eventually 4+ for Ce), but can be lower as demonstrated for Sc_2BC_2 for instance, which can be described in first approximation as being built of $(BC_2)^{5-}$ anions surrounded by not fully oxidized $Sc^{2.5+}$ cations (4). Indeed, the formal charge of 5− was found to be the most favored electron count for an isolated BC_2 unit, corresponding to a large HOMO/LUMO gap separating the low-lying bonding and nonbonding levels from the high-lying antibonding levels. This has been confirmed by extended Hückel (EH) and density functional band calculations (4, 10). The assignment of formal ionic charges for the other nonmetal entities present in $La_{15}B_{14}C_{19}$, $Ce_{10}B_9C_{12}$, $Ce_5B_4C_5$, and $La_5B_2C_6$ is not so straightforward, except for B_5C_6 for which a rather large HOMO/LUMO is computed for the charge of 9−. EH molecular orbital calculations on various B_xC_y units indicate that two or four π-type orbitals of intermediate energy (~9 eV) are lying in the middle of a large energy gap, suggesting the existence of different possible electron counts corresponding to a partial or complete occupation of these intermediate levels (5).

The analysis of the band structure of these compounds calculated within the extended Hückel tight-binding (EHTB) formalism can help in answering the question concerning which ones of these possible electron counts are the closest to the real situation in $La_{15}B_{14}C_{19}$, $Ce_{10}B_9C_{12}$, $Ce_5B_4C_5$, and $Ce_5B_2C_6$. It turns out that in all of these compounds, the states lying around the Fermi level (ε_F) result from the overlap of the bottom of the metallic *d*-band with bands generated by the intermediate MOs of the boron–carbon units. It appears that the intermediate levels of the B_4C_7 unit is calculated to be roughly half-occupied in $La_{15}B_{14}C_{19}$. A similar situation is computed for the B_4C_4 and B_5C_8 chains in $Ce_{10}B_9C_{12}$, for the B_3C_3 and B_4C_4 chains in $Ce_5B_4C_5$, and for the C_2 dumb-bells in $Ce_5B_2C_6$. Consequently, the approximate formal charges for the different finite chains contained in our ternary rare earth metal boron–carbides seem to be $(C_2)^{4-}$, $(BC_2)^{5-}$, $(B_3C_3)^{7-}$, $(B_4C_4)^{8-}$, $(B_5C_6)^{9-}$, and $(B_5C_8)^{9-}$, leading to metal atoms partially oxidized (from 1.73+ in $La_{15}B_{14}C_{19}$ to 2.8+ in $Ce_5B_2C_6$).

Geometry optimization with *ab initio* calculations (11) has been carried out on isolated boron–carbon chains in order to ascertain the boron versus carbon distribution (12) and the proposed assignment of the anionic charges. Bond distances were optimized at the HF and MP2 level using a 6-31G* basis set assuming linear chains. In order to mimic the cationic environment encountered in the solid state, the boron–carbon chains were encapsulated in a cationic field of Na^+ ions described by effective core pseudopotentials (13). Calculations performed for different anionic charges indicate that the best agreement between the optimized and

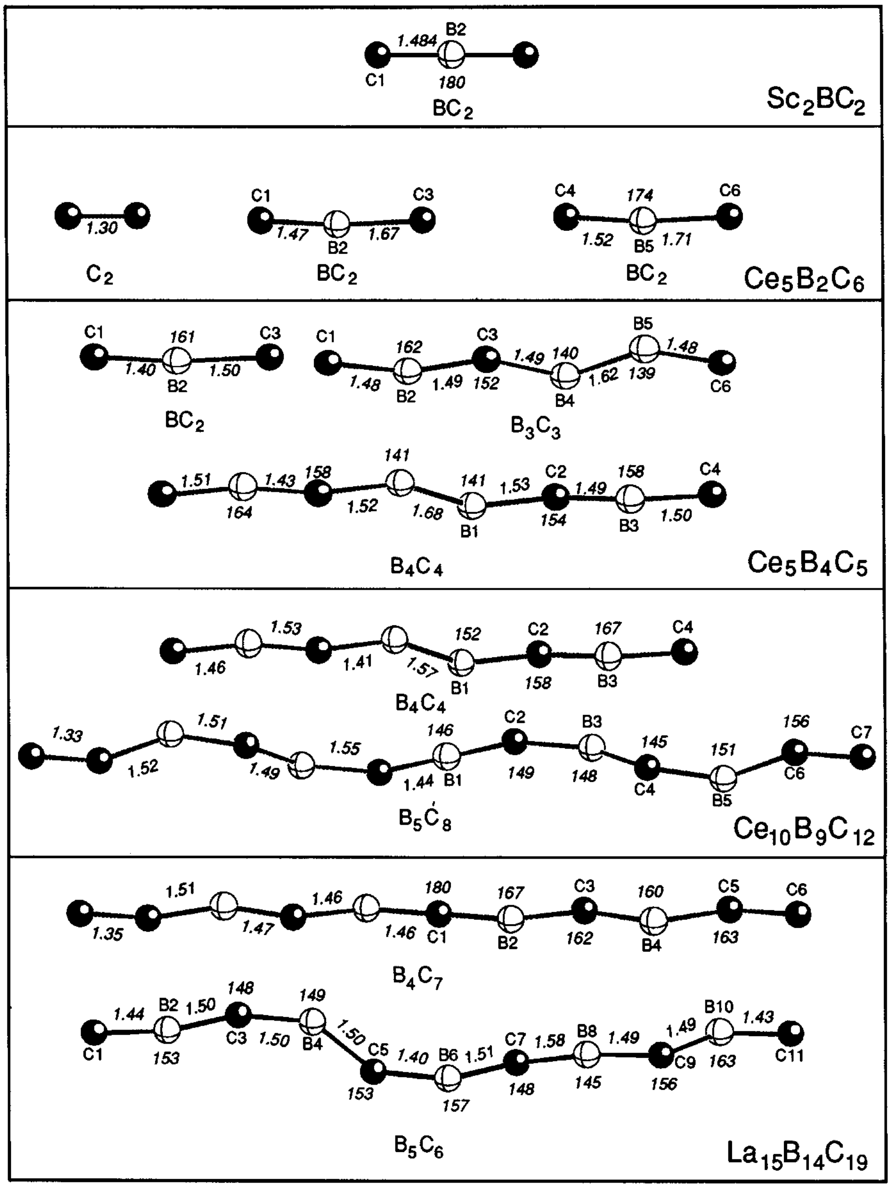

FIG. 2. Various finite boron–carbon chains encountered in ternary $M_xB_yC_z$ compounds. Bond distances (Å) and bond angles (°) are given.

exprimental bond separations is observed for the charges initially proposed on the basis of EH calculations, particularly in the case of the small chains. A comparison between experimental and optimized bond distances for some B_xC_y units is made in Table 2.

A cumulene-like character (formal double bonds along the chains) is confirmed for the proposed charges. This renders them isoelectronic to hypothetical all-carbon cumulenic $(C_n)^{4-}$ molecules which could be represented by Lewis formulae with double C–C bonds and carbon atoms following the octet rule. However, some of them are radical anions if they are linear. Like in the case of O_2, this character cannot be taken into account with classical Lewis formulae.

As shown in Fig. 2, the boron–carbon chains are not rigourously linear. It is known that a small bending of organic cumulene and cumulenone molecules is not costly in energy and is facilitated as they become longer (14). The same phenomenon occurs for the boron–carbon "molecules." For instance, *ab initio* calculations at the MP2 level of theory on a bent and linear $(BC_2)^{5-}$ anion show almost no change in the B–C distances (ca. 1.50 Å) and only a small increase of the total energy (0.59 eV) for a C–B–C bending angle of 150° compared to 180°. Slight C–B–C bending is

TABLE 2
Comparison between Optimized (MP2) and Experimental Bond Distances in Some B_xC_y Units

$(BC_2)^{5-}$	d(C1–B1)[a]				
Calc.	1.494				
Exp. (Sc_2BC_2)	1.484(3)				
Exp. ($Ce_5B_2C_6$)	1.47(6); 1.52(6); 1.67(6); 1.71(6)				
Exp. ($Ce_5B_4C_5$)	1.40(3); 1.50(3)				
$(B_3C_3)^{7-}$	d(C1–B2)	d(B2–C3)	d(C3–B4)	d(B4–B5)	d(B5–C6)
Calc.	1.461	1.497	1.493	1.600	1.442
Exp. ($Ce_5B_4C_5$)	1.48(3)	1.49(3)	1.49(3)	1.62(3)	1.48(2)
$(B_4C_4)^{8-}$	d(B1–B1′)	d(B1–C2)	d(C2–B3)	d(B3–C4)	
Calc.[b]	1.582	1.434	1.543	1.459	
Exp. ($Ce_{10}B_9C_{12}$)	1.57(3)	1.41(2)	1.53(2)	1.46(2)	
Exp. ($Ce_5B_4C_5$)	1.68(3)	1.53(3)	1.49(3)	1.50(3)	
		1.52(3)	1.43(3)	1.51(3)	
$(B_5C_6)^{9-}$	d(C1–B2)	d(B2–C3)	d(C3–B4)	d(B4–C5)	d(C5–B6)
Calc.	1.413	1.495	1.409	1.443	1.411
Exp. ($La_{15}B_{14}C_{19}$)	1.44(3)	1.50(3)	1.50(3)	1.50(3)	1.40(3)
	d(B6–C7)	d(C7–B8)	d(B8–C9)	d(C9–B10)	d(B10–C11)
Calc.	1.411	1.443	1.409	1.495	1.413
Exp. ($La_{15}B_{14}C_{19}$)	1.51(3)	1.58(3)	1.49(3)	1.49(3)	1.43(3)
$(B_4C_7)^{8-}$	d(C1–B2)	d(B2–C3)	d(C3–B4)	d(B4–C5)	d(C5–C6)
Calc.[c]	1.419	1.424	1.434	1.454	1.319
Calc.[d]	1.415	1.425	1.442	1.437	1.332
Exp. ($La_{15}B_{14}C_{19}$)	1.46(3)	1.46(3)	1.47(3)	1.51(3)	1.35(3)
$(B_5C_8)^{9-}$	d(B1–C2)	d(C2–B3)	d(B3–C4)	d(C4–B5)	d(B5–C6)
Calc.[c,e]	1.431	1.450	1.418	1.439	1.443
Calc.[d,e]	1.425	1.477	1.395	1.479	1.434
Exp. ($Ce_{10}B_9C_{12}$)	1.44(1)	1.55(2)	1.49(2)	1.51(2)	1.50(2)
	d(C6–C7)				
Calc.[c,e]	1.284				
Calc.[d,e]	1.308				
Exp. ($Ce_{10}B_9C_{12}$)	1.33(2)				

[a] See Fig. 2 for the labeling.
[b] Triplet state.
[c] Singlet state.
[d] Quintuplet state.
[e] HF level of theory.

present in $Ce_5B_2C_6$. A rather more important bending (C–B–C = 147.8(3)°) is observed for the $(BC_2)^{5-}$ units contained in $La_3Br_2BC_2$ (15). Larger distortion is experimentally observed for the longest B–C chains (see Fig. 2). Small constraints of the surrounding metallic matrix must be sufficient to allow a small distortion of the B–C chains without modifying too much their electronic structure.

CONCLUSION

The analysis of the bonding in the rare earth metal boron carbides encapsulating finite boron–carbon chains with the help of EH and *ab initio* calculations has shown that the structural arrangement of the boron–carbon sublattice can be explained roughly with an ionic bonding picture. Such an approach can be extended to other solid state compounds containing such nonmetal entities. Just mentioning some ternary or quaternary rare earth metal compounds, $(BC_2)^{5-}$ and $(B_2C_2)^{6-}$ chains are present in $La_3Br_2BC_2$ and $Ce_6Br_3B_2C_3$, respectively (15), $(B_2C)^{2-}$ groups are encapsulated in $LuNi_2B_2C$ (16), and $(BN_3)^{6-}$, $(B_2N_4)^{8-}$, and $(B_3N_6)^{9-}$ "molecular" units are contained in $Ce_{15}B_8N_{25}$ (17), $Ce_3B_2N_4$ (18), and $PrBN_2$ (19), respectively. The bonding analysis of the latter, the rare earth metal boron nitrides, is in progress in our laboratory (20).

Such an ionic picture cannot explain the physical properties observed for this kind of material. Band calculations carried out on these compounds have shown that a significant covalent interaction occurs between the metallic framework and the boron–carbon "ligands" (5). Such an interaction is associated with some electron transfer from the occupied levels of the boron–carbon chains into empty levels of the metallic *d*-band. This reduces somewhat the anionic charge on the boron–carbon molecules trapped in the metallic matrix, participating consequently in their stabilization. With the metal atoms not fully oxidized and their band structures exhibiting a Fermi level cutting rather important peaks of density of states made of metal and boron–carbon contributions, all these rare earth metal boron carbide materials are expected to exhibit metallic properties. Some of them such as $La_5B_2C_6$ are even superconducting at low temperture (21).

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