Planar B_6 Ring

DOI: 10.1002/anie.201106798

All-Boron Planar B_6 Ring in the Solid-State Phase $Ti_7Rh_4Ir_2B_8$**

Boniface P. T. Fokwa and Martin Hermus*

Planar rings built up by one chemical element have been the focus of experimental and theoretical work in the molecular and inorganic solid-state chemistry, with carbon building such planar units more than any other element.[1–5] However, elements in the same group of the periodic table as carbon were also found to build such ring-type substructures, for example the flat pentagonal rings of Sn_5^{6-} and Pb_5^{6-} found in Na_8BaSn_6 (or Na_8EuSn_6) and Na_8BaPb_6, respectively, by Sevov and Todorov.[6] Having only one valence electron less than these elements, boron is known to build mainly cage substructures (polyhedra), such as those found in elemental boron structures,[1] boranes,[4] or boron-rich compounds;[7] boron also builds fragments (dumbbells, chain fragments, trigonal planar units, or tetrahedra) that occur mainly in boron-poor compounds.[8,9] Consequently planar boron rings are almost inexistent. According to our literature survey, there are only three compounds containing such entities: Fehlner et al.[10a,b] reported on the syntheses and crystal structures of two triple-decker sandwich complexes containing planar B_5Cl_5 and $B_6H_4Cl_2$ structural fragments, and Himmel et al. have just published the doubly base-stabilized $B_3H_6^+$ analogue accommodating a planar boron triangle in a triborane complex.[10c] Nearly all studies on these planar boron rings are either theoretical or gas-phase experiments.[11] Nevertheless, the large amount of works in this field clearly shows the potential of such types of boron fragments. As mentioned by Wang et al. in their Review,[11a] pure planar boron clusters are promising molecules for coordination chemistry as potential new ligands and for materials science as new building blocks. The absence of planar B_6 rings in solid-state phases is very surprising, given the fact that such an entity is the fundamental starting motif for the generation of the boron layers found in the crystal structures of the rich family of AlB_2-type compounds which includes the superconducting MgB_2[12] and the mechanically hard, high-melting and chemically inert TiB_2.[13]

Herein we report about the synthesis, crystal structure, first-principles density functional theory (DFT) analysis, and bonding analysis of the novel solid-state boride $Ti_7Rh_4Ir_2B_8$ which as well as the aforementioned planar B_6 ring, also contains one-dimensional chains of Ti_7 wheels and one-dimensional strings of face-sharing empty tetrahedral and square-pyramidal clusters.

The crystal structure of the title compound (a variant of the recently discovered $Ce_7Ni_{5\pm x}Ge_{3\pm x}In_6$ structure type)[14] was determined by single-crystal X-ray diffraction and is composed of two alternating layers stacked along the *c* axis. The first layer at $z = 0$ contains the Ti_7 wheels and isolated boron atoms whereas the second layer at $z = \frac{1}{2}$ is filled with M atoms ($M = 2/3\,Rh + 1/3\,Ir$) and the planar B_6 rings (see Figure 1).

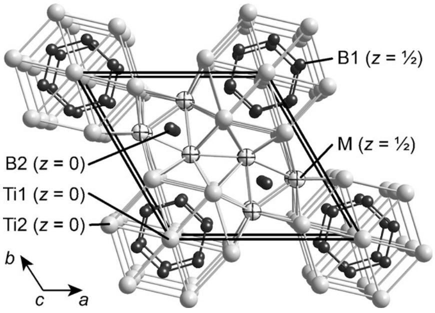

Figure 1. Projection of the structure of $Ti_7Rh_4Ir_2B_8$ along [001]. The two different layers ($z = 0$ and $z = \frac{1}{2}$) are indicated: $M = 2/3\,Rh + 1/3\,Ir$.

There are two different crystallographic sites for the boron atoms (B1 at 6*k* and B2 at 2*c*), which have different coordination environments and are found in different layers: B1 forms the planar B_6 ring and is coordinated by six titanium atoms, in a trigonal prismatic manner, with all three rectangular faces capped (two by B1 atoms and one by an M atom), whereas the B2 atom resides in a trigonal prism built up by six M atoms and capped by three Ti2 atoms. Titanium is also found in two different Wyckoff sites (Ti1 at 1*a* and Ti2 at 6*j*) and thus also has two different coordination environments: Ti1 has the same environment as the titanium atoms in TiB_2 (AlB_2-type structure) namely a twelve coordination by boron atoms (B1) to form a regular hexagonal prism (see Figure 2a). Ti2 is coordinated by six M atoms and four B1 atoms in a distorted pentagonal prismatic manner with three rectangular faces each capped by one Ti atom (one by Ti1 and two by Ti2 atoms). The M atoms ($M = 2/3\,Rh + 1/3\,Ir$) are coordinated by six titanium (Ti2) and two boron atoms (B2), in a distorted tetragonal prismatic manner with three faces capped by M atoms.

Three interesting features are seen in the crystal structure of $Ti_7Rh_4Ir_2B_8$: one-dimensional chains of planar Ti_7 wheels, one-dimensional strings of face-sharing empty tetrahedral and square-pyramidal clusters and, most importantly, planar B_6 rings (Figure 1).

Note that the one-dimensional chains of stacked Ti_7 wheels cannot be regarded as seven interconnected one-

---

[*] Priv.-Doz. Dr. B. P. T. Fokwa, Dipl.-Chem. M. Hermus
Institute of Inorganic Chemistry, RWTH Aachen University
Landoltweg 1, 52056 Aachen (Germany)
E-mail: boniface.fokwa@ac.rwth-aachen.de
Homepage: http://www.ssc.rwth-aachen.de/fokwa

[**] We thank Deutsche Forschungsgemeinschaft for financial support (Heisenberg fellowship to B.P.T.F.) and Resi Zaunbrecher (IPC, RWTH Aachen) for the EDX analyses.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201106798.

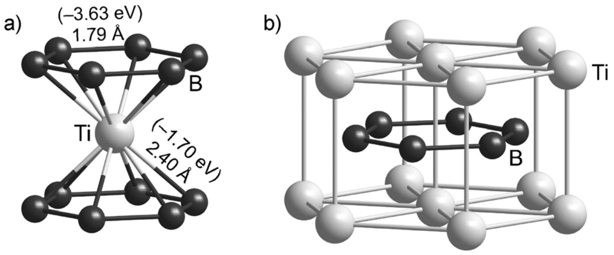

Figure 2. Parts of the crystal structure of $Ti_7Rh_4Ir_2B_8$ showing a) the one-dimensional B_6TiB_6 entity with B–B and Ti–B bond lengths and corresponding ICOHP values and b) two planar Ti_7 wheels with a planar B_6 ring lying between them.

dimensional Ti chains, because the Ti–Ti bonds within the Ti_7 unit are stronger (see bonding analysis below) than those between them (along [001]), thus the Ti_7 units can be viewed as a fragment of the TiB_2 structure. These Ti_7 chains are, to our knowledge, the first observed for any 3d transition metal in metal borides. However, simple one-dimensional titanium chains are common entities in phases of this compound family. Interestingly, when these simple Ti chains are substituted by chains of magnetically active elements (Cr, Mn, Co, Fe, Ni) itinerant magnets (antiferro-, ferri-, and ferromagnets) are produced in the process, as was done for example in $Ti_2Fe(Ru/Rh)_5B_2$ and $Ti_{9-n}Fe_{2+n}Ru_{18}B_8$ phases.[15–17] It is therefore possible to achieve such magnetic properties by substituting some (or all) titanium atoms of the Ti_7 wheels by magnetically active elements. In fact, according to the rigid band analysis below, up to four valence electrons may be added (e.g. substitution of one Ti by Fe) to this structure without destabilizing it.

The second interesting feature of $Ti_7Rh_4Ir_2B_8$ is the one-dimensional chain of face-sharing empty tetrahedral and square-pyramidal $(Ti/M)_6$ clusters running along the [001] direction (Figure 1). This entity was also found in $Ti_{1.6}Os_{1.4}RuB_2$-type phases but built up by different metals.[9b,c] A similar chain of clusters, built up by face-sharing octahedra, however, was found in compounds with the Th_7Fe_3 structure type. We believe that these types of channels were unconsciously used in the Pauli paramagnetic Th_7Fe_3 to host hydrogen and improve the magnetic properties of the binary parent compound, as its hydrogenation leads to the ferromagnetic $Th_7Fe_3H_{30}$.[18] In fact, the hydrogenation of many other intermetallic compounds frequently results in a striking alteration of their electronic and magnetic characteristics and leads to some extraordinary new features.[19]

The third and most fascinating feature of the novel compound is of course the planar B_6 ring. To our knowledge no other solid-state phase containing such a fragment has been reported. As mentioned above, only one molecular-based compound (a sandwich complex) is known to contain such a planar B_6 ring, which is, however, further connected to hydrogen and chlorine atoms.[10a,b] Nonetheless, the occurrence of such a planar B_6 ring in metal borides may have been expected because it can be considered the starting motif to generate the boron layer (graphene analogue) in the AlB_2-type structure.

The chemical bonding in $Ti_7Rh_4Ir_2B_2$ was analyzed by first-principles density functional theory (DFT) using the COHP method and its energy integral (ICOHP; Figure 3). All interatomic distances in the crystal structure and their corresponding ICOHPs compare quite well with those values already found in previous transition-metal borides (see Table 1).[16,17,20a,b] We will therefore focus our attention on the bonding situation in the two novel entities present in this crystal structure: The planar B_6 ring and the chains of stacked Ti_7 wheels.

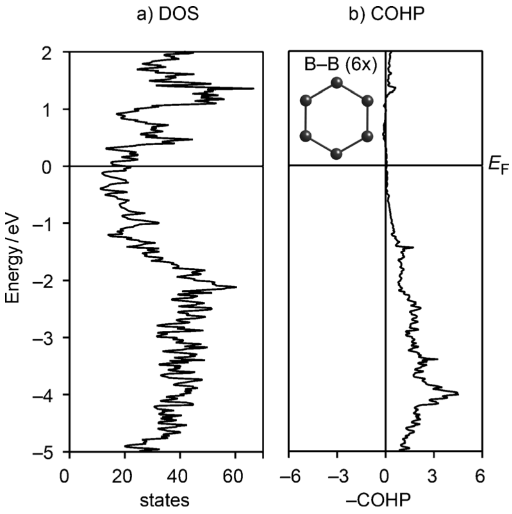

Figure 3. a) Theoretical density-of-states (DOS) of $Ti_7Rh_4Ir_2B_8$ and b) COHP curve of the B–B interactions in the planar B_6 ring. The Fermi level (E_F) has been set to the energy zero.

The B1–B1 distance (1.79 Å) is very close to the bond found in TiB_2 (1.75 Å)[20a] and comparable even with those

Table 1: Selected bond lengths (single-crystal results) and ICOHP values for $Ti_7Rh_4Ir_2B_8$ and related examples.[20a,b]

Bond	Length [Å]	ICOHP [eV]	Example	Length [Å]	ICOHP [eV]
B1–B1 (B_6 unit)	1.79(3)	−3.631	TiB_2	1.749	−4.035
Ti1–B1 (B_6TiB_6 sandwich)	2.40(2)	−1.696	TiB_2	2.380	−1.809
Ti2–B1 (Ti_6 and B_6 rings)	2.32(2)–2.35(2)	−2.034	TiB_2	2.380	−1.809
Ti–Ti (within Ti_7 wheel)	2.996(5)	−0.933	TiB_2	3.030	−0.945
Ti1–Ti1 along [001]	3.1965(8)	−0.513	TiB_2	3.229	−0.450
Ti2–Ti2 along [001]	3.1965(8)	−0.670	TiB_2	3.229	−0.450
M–B2 (in trigonal prisms)	2.230(1)	−2.662	$Ti_3Ru_3Ir_2B_2$	2.186	−2.885
M–B1 (B_6 unit)	2.37(2)	−1.674	–	–	–
M–Ti2	2.682(4)–2.860(3)	−1.631	$Ti_3Ru_3Ir_2B_2$	2.847	−1.464
M–M	2.693(2)–3.196(1)	−0.924	$Ti_3Ru_3Ir_2B_2$	2.926	−0.809

found in the molecular-complex-based planar B_5Cl_5 (1.69–1.79 Å)[10b] and $B_6H_4Cl_2$ (1.70–1.78 Å)[10b] fragments. Therefore the B1−B1 bond is expected to be strong. The COHP analysis confirms very strong B1−B1 bonding interactions (Figure 3b), with an energy integral (ICOHP) of −3.63 eV per bond which is the highest in this structure and is just slightly lower than the calculated value (−4.04 eV per bond) for the same type of interaction in TiB_2.

The strong B1−B1 bonding interactions weaken the Ti−B bonds for which an average ICOHP value of −1.87 eV per bond is found, which however is still slightly larger than the value (−1.81 eV/bond) found in TiB_2, and is as expected on the basis of the B1−B1 bond strength. The strength of the B1−B1 bonding results in only weak metallic Ti−Ti bonding, with the highest ICOHP value (−0.93 eV per bond) found in the Ti_7 wheels, this value which is much higher than the average value (−0.59 eV per bond) calculated between the stacked wheels (along [001]). The same Ti−Ti bonding situation is found in TiB_2 (see Table 1) so that this part of the new structure (see Figure 2b) can be regarded as a one-dimensional building block for the TiB_2 structure. Because of the finite density of states (DOS) at the Fermi level (Figure 3a), the phase is predicted to be a metal, as expected for this metal-rich phase. Furthermore a large pseudo gap is observed between approximately −1.3 eV below and approximately 0.4 eV above the Fermi edge (E_F) which indicates that some valence electrons (VE) may be removed (ca. 11 VE) or added (ca. 4 VE) to this crystal structure without destabilizing it. This type of prediction has been very successful in similar phases:[9b–d,17,20b] For example, the syntheses of the ferrimagnetic $Ti_{9-n}Fe_{2+n}Ru_{18}B_8$ ($n=1$, 2) phases were guided by a prediction made from the $Ti_9Fe_2Ru_{18}B_8$ ferromagnet, by adding more electrons to the later through substituting titanium for the electron richer iron.[17] Consequently even more phases containing the rare planar B_6 ring as well as new itinerant magnetic phases adopting the same structure as $Ti_7Rh_4Ir_2B_8$ should be expected.

Experimental Section

Needle-shaped silvery single crystals of $Ti_7Rh_4Ir_2B_8$ were synthesized by arc-melting high purity elements (at least 99.9%, starting ratio, 3:3:1:3) in a water-cooled copper crucible under an argon atmosphere using a tungsten tip as a second electrode. For details concerning the synthetic steps see Ref. [20b] A silver-like product with metallic luster was obtained with several single crystals suitable for X-ray structure analysis. The powder diffractogram of the product shows beside the reported phase also a side phase crystallizing with the double perovskite Ti_2Rh_6B-type.[20c]

Crystal data of $Ti_7Rh_4Ir_2B_8$: hexagonal, $a=9.196(2)$, $c=3.0336(7)$ Å, $V=234.11(8)$ Å^3, $T=293(2)$ K, space group $P6m$ (no. 175) which is the highest space group found from the diffraction data, $Z=1$; diffraction data collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromatized $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å), empirical absorption correction with SADABS,[21] 4801 reflections measured, 412 unique ($R_{int}=0.075$). The final values for R_1 and wR_2 (all 412 data, 21 parameters) were 0.056 and 0.097, respectively. Crystal structure solution/refinement by means of SHELX programs.[22] Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-423590. The crystallographic data collected for two single crystals provided identical chemical compositions and the metals ratio were confirmed by EDX analyses on several crystals (1/2.04/3.54 for Ir/Rh/Ti, averaged experimental data) using a high-resolution low-energy SEM of the type LEO/Zeiss 1450 VP (Oberkochen, Germany) equipped with an EDX system of the type INCA (Oxford, England).

All electronic-structure calculations were based on the all-electron scalar-relativistic Linear Muffin-Tin Orbital (LMTO) theory[23] in its tight-binding representation[24] using the TB-LMTO-ASA 4.7 code.[25] The exchange-correlation contributions to the total energies were treated in the generalized gradient approximation (GGA) using the Perdew and Wang parameterization potential.[26] Self-consistency was achieved when the total-energy change was smaller than 1×10^{-5} Ry. The chemical bonding situations were analyzed using the Crystal Orbital Hamilton Population (COHP) technique[27] as implemented in the TB-LMTO-ASA program package.

Received: September 24, 2011

Keywords: bonding · borides · boron rings · solid-state chemistry · titanium wheels

---

[1] N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, 2nd ed., Butterworth–Heinemann, Oxford, **1997**.
[2] F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, 6th ed., Wiley, New York, **1999**.
[3] R. B. King, *Chem. Rev.* **2001**, *101*, 1119.
[4] E. D. Jemmis, M. N. Balakrishnarajan, P. D. Pancharatna, *Chem. Rev.* **2002**, *102*, 93.
[5] P. von R. Schleyer, Guest Editor (introduction to the thematic issue on Aromaticity), *Chem. Rev.* **2001**, *101*, 1115.
[6] I. Todorov, S. C. Sevov, *Inorg. Chem.* **2004**, *43*, 6490.
[7] "Higher Borides": T. Mori in *Handbook on the Physics and Chemistry of Rare Earths, Vol. 38* (Eds.: K. A. Gschneidner, Jr., J.-C. Bunzli, V. Pecharsky), Elsevier, Amsterdam, **2008**.
[8] E. Wiberg, N. Wiberg, A. F. Holleman, *Inorganic chemistry*, Academic Press, San Diego, **2001**.
[9] a) H. Hillebrecht, M. Ade, *Angew. Chem.* **1998**, *110*, 981; *Angew. Chem. Int. Ed.* **1998**, *37*, 935; b) B. P. T. Fokwa, J. von Appen, R. Dronskowski, *Chem. Commun.* **2006**, 4419; c) B. P. T. Fokwa, R. Dronskowski, *Z. Anorg. Allg. Chem.* **2008**, *634*, 1955; d) B. P. T. Fokwa, *Eur. J. Inorg. Chem.* **2010**, 3075; e) M. Ade, D. Kotzot, H. Hillebrecht, *J. Solid State Chem.* **2010**, *183*, 1790.
[10] a) S. Ghosh, A. M. Beatty, T. P. Fehlner, *J. Am. Chem. Soc.* **2001**, *123*, 9188; b) B. Le Guennic, H. Jiao, S. Kahlal, J.-Y. Saillard, J.-F. Halet, S. Ghosh, M. Shang, A. M. Beatty, A. L. Rheingold, T. P. Fehlner, *J. Am. Chem. Soc.* **2004**, *126*, 3203; c) N. Schulenberg, H. Wadepohl, H.-J. Himmel, *Angew. Chem.* **2011**, *123*, 10628; *Angew. Chem. Int. Ed.* **2011**, *50*, 10444.
[11] a) A. N. Alexandrova, A. I. Boldyrev, H.-J. Zhai, L. S. Wang, *Coord. Chem. Rev.* **2006**, *250*, 2811; b) Z. Pu, K. Ito, P. v. R. Schleyer, Q.-S. Li, *Inorg. Chem.* **2009**, *48*, 10679; c) C. Romanescu, T. R. Galeev, W.-L. Li, A. I. Boldyrev, L.-S. Wang, *Angew. Chem.* **2011**, *123*, 9506; *Angew. Chem. Int. Ed.* **2011**, *50*, 9334.
[12] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, J. Akimitsu, *Nature* **2001**, *410*, 63.
[13] P. Schwartzkopf, R. Kieffer, *Refractory Hard Metals: Borides, Carbides, Nitrides and Silicides*, Macmillan, New York, **1953**.
[14] N. Chumalo, G. P. Nychyporuk, V. V. Pavlyuk, R. Pöttgen, D. Kaczorowski, V. I. Zaremba, *J. Solid State Chem.* **2010**, *183*, 2963.

[15] a) B. P. T. Fokwa, H. Lueken, R. Dronskowski, *Chem. Eur. J.* **2007**, *13*, 6040; b) B. P. T. Fokwa, H. Lueken, R. Dronskowski, *Eur. J. Inorg. Chem.* **2011**, 3926.
[16] B. P. T. Fokwa, G. D. Samolyuk, G. J. Miller, R. Dronskowski, *Inorg. Chem.* **2008**, *47*, 2113.
[17] a) C. Goerens, J. Brgoch, G. J. Miller, B. P. T. Fokwa, *Inorg. Chem.* **2011**, *50*, 6289; b) J. Brgoch, C. Goerens, B. P. T. Fokwa, G. J. Miller, *J. Am. Chem. Soc.* **2011**, *133*, 6832.
[18] a) E. B. Boltich, S. K. Malik, T. Takeshita, *Solid State Commun.* **1978**, *28*, 359; b) E. B. Boltich, S. K. Malik, W. E. Wallace, *J. Less-Common Met.* **1980**, *74*, 111.
[19] F. Pourarian, *Physica B* **2002**, *321*, 18.
[20] a) B. P. T. Fokwa, P. R. N. Misse, M. Gilleßen, R. Dronskowski, *J. Alloys Compd.* **2010**, *489*, 339; b) B. P. T. Fokwa, M. Hermus, *Inorg. Chem.* **2011**, *50*, 3332; c) B. P. T. Fokwa, B. Eck, R. Dronskowski, *Z. Kristallogr.* **2006**, *221*, 445.
[21] SADABS. (Version 2.03), SHELXTL (Version 6.12), Bruker **2001**.
[22] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112.
[23] a) O. K. Andersen, *Phys. Rev. B* **1975**, *12*, 3060; b) H. Skriver, *The LMTO Method*, Springer, Berlin, **1984**.
[24] O. K. Andersen, O. Jepsen, *Phys. Rev. Lett.* **1984**, *53*, 2571.
[25] G. Krier, O. Jepsen, A. Burkhardt, O. K. Andersen, *The TB-LMTO-ASA program, version 4.7*, Max Planck Institute for Solid-State Research, Stuttgart, Germany.
[26] J. P. Perdew, Y. Wang, *Phys. Rev. B* **1992**, *45*, 13244.
[27] a) R. Dronskowski, P. E. Blöchl, *J. Phys. Chem.* **1993**, *97*, 8617; b) R. Dronskowski, *Computational Chemistry of Solid State Materials*, Wiley-VCH, Weinheim, New York, **2005**.