Synthesis of a missing structural link: the first trigonal planar B_4 units in the novel complex boride $Ti_{1+x}Os_{2-x}RuB_2$ ($x = 0.6$)

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The newly synthesized boride $Ti_{1+x}Os_{2-x}RuB_2$ ($x = 0.6$) has a novel structure featuring one-dimensional chains of titanium atoms, one-dimensional strings of face-sharing empty tetrahedral and square pyramidal clusters and, most importantly, trigonal planar and strongly bonded B_4 units with a B–B distance of 1.89 Å.

Metal borides have been intensively investigated up to the present day because of their fascinating crystal structures and, in particular, physical properties such as mechanical hardness, magnetism or superconductivity. Their structures usually contain isolated but also interconnected boron atoms, leading to the formation of three-dimensional boron *networks* (*e.g.*, in CaB_6), boron *layers* (*e.g.*, in AlB_2), boron *chains* (*e.g.*, in PtB)—all of which have become textbook knowledge—or other boron fragments. The most common boron fragment found in metal borides is a dumbbell (boron pair).[1,2] Moreover, *linear* B_4 chain fragments were found in Rh_5B_4 and Mo_2IrB_2,[2,3] whereas *cis–trans* chain-like B_6 fragments occur in Rh_3B_{2-x}.[4] Although nearly all boron layers and even the boron chain present in $Ru_{11}B_8$ can be thought of as being constructed from a trigonal planar B_4 fragment,[5] such a boron "missing link" in terms of structure has never been reported, neither in borides nor in other intermetallic phases.

Herein we report about the synthesis and crystal structure of the novel complex boride $Ti_{1+x}Os_{2-x}RuB_2$ ($x = 0.6$) which does not only exhibit the aforementioned trigonal planar B_4 fragment, but also one-dimensional titanium chains and one-dimensional strings of face-sharing empty tetrahedral and square pyramidal clusters.

The crystal structure of the title compound was determined by single-crystal X-ray diffraction† and is composed of two alternating layers stacked along the *c* axis. The first layer contains the M1 atoms (69% Os + 31% Ti) and the trigonal planar B_4 fragments (containing B1 and B2 atoms), and the second layer is filled with ruthenium atoms, M2 atoms (96% Ti + 4% Os) and isolated boron atoms (B3). Although the two layers exhibit mixed atomic positions (M1 and M2) by osmium and titanium, there is an obvious site-preferential tendency. It is the osmium atoms which mainly enter the layer at $z = ½$ whereas the titanium atoms are mostly found in the layer at $z = 0$. The two layers are interconnected, mainly by M1–M1, M1–Ru, and Ru–Ru bonds, thereby generating the coordination environments around the boron and the M2 atoms (see Fig. 1).

There are three different crystallographic sites found for the boron atoms (B1 at 1*b*, B2 at 3*g*, and B3 at 2*c*), which are thus located in different coordination environments: B1 is coordinated by six ruthenium atoms, in a trigonal prismatic manner, with all three rectangular faces capped by B2 atoms, whereas the B2 atom is incorporated in an elongated trigonal prism of four ruthenium and two M1 atoms, with just one rectangular face capped by a B1 atom. It is only the B3 atom which resides in an uncapped trigonal prism built up by six M1 atoms. The polyhedra around B1 and B3 are stacked on top of each other (sharing one face) along the [001] direction, whereas the one around B2 only shares one edge along the [001] direction because it alternates with another elongated trigonal prism (four M2 + two Ru) which remains empty. Ruthenium is coordinated by four M1, two other ruthenium and four boron atoms (B2) in a distorted pentagonal prismatic manner with two rectangular faces capped by boron atoms (B1). The M2 atoms (mainly titanium, 96%) are coordinated by eight M1 (mainly osmium, 69%) and two boron atoms (B2), also in a distorted pentagonal prismatic manner. The M1 atoms are surrounded by two ruthenium, three boron (one B2 and two B3), four M2 and three other M1 atoms to result in a strongly distorted icosahedron.

There are three interesting features seen in the structure of $Ti_{1.6}Os_{1.4}RuB_2$ (Fig. 2): one-dimensional M2 (96% Ti + 4% Os) chains, one-dimensional strings of face-sharing empty tetrahedral and square pyramidal clusters and, most importantly, trigonal planar B_4 fragments.

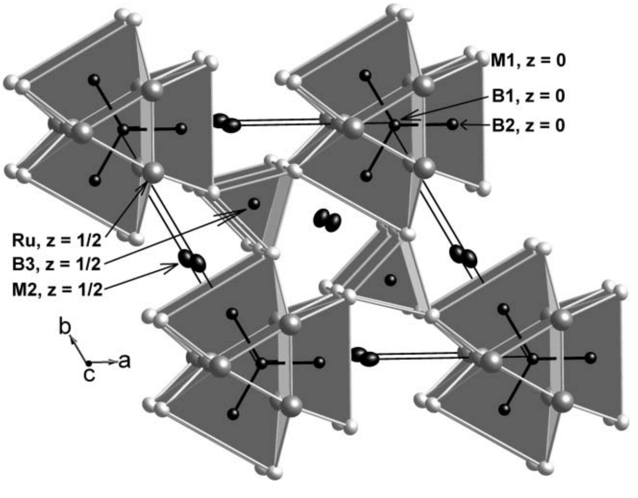

Fig. 1 Projection of the structure of $Ti_{1.6}Os_{1.4}RuB_2$ along [001]. Boron-centered trigonal prisms are highlighted: M1 = 69% Os + 31% Ti, M2 = 96% Ti + 4% Os.

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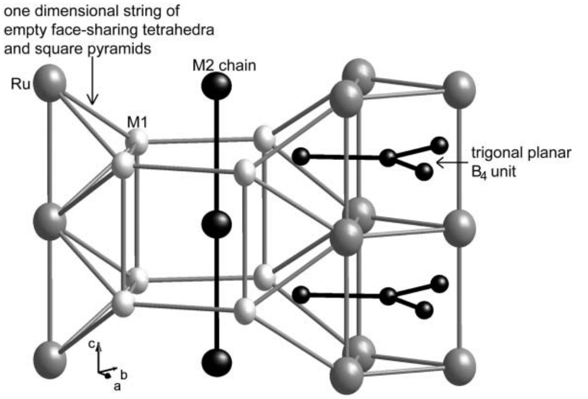

Fig. 2 The three structural features of $Ti_{1.6}Os_{1.4}RuB_2$: one-dimensional strings of face-sharing empty tetrahedral and square pyramidal $(Ru/M1)_6$ clusters running along [001], one-dimensional chains of M2 atoms also running along [001] and the trigonal planar B_4 units: M1 = 69% Os + 31% Ti, M2 = 96% Ti + 4% Os.

It is worthwhile noting that the one-dimensional M2 chain (96% Ti + 4% Os) found here is not new but has also been observed for all 3*d* elements in related phases of the $Ti_3Co_5B_2$ structure type. In both cases the intra-chain metal distances are almost the same ($\approx$3.0 Å), whereas the inter-chain distances come out smaller (4.6 Å) for $Ti_{1.6}Os_{1.4}RuB_2$ than for the compounds of the $Ti_3Co_5B_2$ type ($\approx$6.6 Å). Nonetheless, it may well be possible that substituting the M2 site by a magnetically active element (such as Mn, Fe, Co, Ni) could have the same consequence for the magnetic behavior of these hypothetical compounds as for those of the $Ti_3Co_5B_2$ type which were all found to behave as itinerant magnets (antiferro-, meta- and ferromagnetism).[6]

The second interesting feature of $Ti_{1.6}Os_{1.4}RuB_2$ is the one-dimensional chain made of face-sharing empty tetrahedral and square pyramidal $(Ru/M1)_6$ clusters running along the [001] direction. The tetrahedra are built up of two M1 and two Ru atoms while the square pyramids are constructed of four planar M1 atoms and one apical Ru atom (Fig. 2). A similar chain of clusters, built up by face-sharing octahedra, however, was found in compounds with the Th_7Fe_3 structure type.[7] We believe that these channels were used, unconsciously so, 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 compound $Th_7Fe_3H_{30}$ which is a ferromagnet.[8] 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.[9]

The third and most fascinating feature of the novel compound is the trigonal planar B_4 fragment. To the best of our knowledge, $Ti_{1.6}Os_{1.4}RuB_2$ is the first intermetallic compound containing such a B_4 fragment. Two examples of a related trigonal planar unit were found for the elements *silicon* and *germanium* in the Zintl phases $Li_{12}Si_7$ and $M_{5+x}Mg_{18-x}E_{13}$ (M = Sr, Ba; E = Si, Ge)[10,11] but usually the observed X_4 units (X = any element) in intermetallic phases or in other ionic compounds are *not* trigonal planar. For example, B_4 *chains* are observed in Rh_5B_4 and Mo_2IrB_2, As_4^{4-} or Sb_4^{4-} *squares* are found in arsenides and antimonides, respectively,[12] and even in the very rich structural chemistry of polysulfides the S_4^{2-} units are *zigzag*-like.[13] A trigonal planar arrangement, however, is commonly found by combining at least two elements (XY_3), *e.g.*, the boron trihalogenides BZ_3 (Z = F, Cl, Br, I) or the complex ions BO_3^{3-}, BN_3^{6-} and CO_3^{2-} which are all trigonal planar. On the other hand, the occurrence of such a B_4 fragment in metal borides is not exceedingly surprising because nearly all boron *layers* and even the boron *chain* present in $Ru_{11}B_8$ can be thought of as being constructed from a trigonal planar B_4 unit as exemplified for the case of the boron layer found in the MgB_2 superconductor (Fig. 3).[1,14]

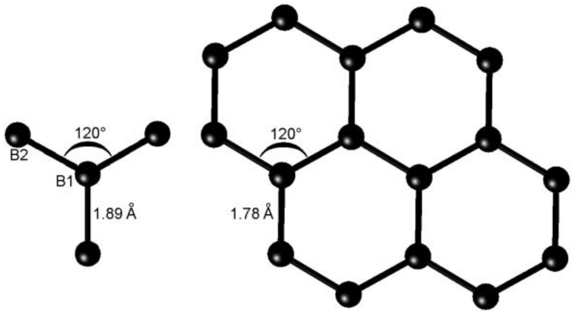

Fig. 3 The trigonal planar B_4 fragment in $Ti_{1.6}Os_{1.4}RuB_2$ (left) is the fundamental starting motif for generation of the boron layer structure in MgB_2 (right).

The interatomic distances in the structure of $Ti_{1.6}Os_{1.4}RuB_2$ (see Table 1) compare quite well with those values already found in previous transition-metal borides. The metal–boron distances vary between 2.16 and 2.37 Å, with Ru–B1 (2.16 Å) being the shortest one and similar to those found in the phases Ru_2B_3 (average 2.18 Å)[15] and $Fe_xRu_{7-x}B_3$ ($0 < x \leqslant 1.5$, average 2.14 Å).[16] In addition, the distance is just slightly wider (0.08 Å) than the sum of the covalent radii (2.08 Å) and thus alludes to a relatively strong bond. This distance is followed by the M1–B (M1 = 69% Os + 31% Ti) distances (2.21 and 2.34 Å), with an average value of 2.27 Å which is also wider than the average sum of the covalent radii, 2.14 Å (*i.e.*, 2.10 Å for Os–B, and 2.18 Å for Ti–B). The Ru–B2 and M2–B2 (M2 = 96% Ti + 4% Os) distances are even larger, namely 2.31 and 2.37 Å. All metal–metal distances (Ru–Ru, Ru–M1, and M1–M1, which vary from 2.66 to 2.78 Å) are within the expected ranges, and they nearly equal those found in RuOs (between 2.66 and 2.72 Å).[17]

The B1–B2 distance (1.89 Å) is just 0.07 Å larger than the average distance observed in α-boron ($\approx$1.82 Å).[1,18] Much wider distances (up to 2.22 Å) were reported in other related borides, *e.g.*, in Rh_3B_{3-x}, Rh_5B_4 and also MOs_3B_4 (M = Mg, Sc)[9,10,19] such that the B–B distance in the trigonal planar B_4 unit is expected to be a strong bond. The COHP analysis confirms very strong bonding

Table 1 Selected bond lengths (Å) and angles (°) in $Ti_{1.6}Os_{1.4}RuB_2$[a]: M1 = 69% Os + 31% Ti, M2 = 96% Ti + 4% Os

Ru	–B1	2.160(2)	M2	–B2	2.37(2)
	–B2	2.31(2)		–B3	2.655(2)
	$–Ru^{ii}$	2.663(4)		–M2	3.034(1)
	–M1	2.720(2)	B1	–B2	1.89(3)
M1	–B3	2.207(1)			
	–B2	2.34(2)	$B2–B1–B2^{ii}$		120
	$–M1^{i}$	2.728(2)	$M2^{i}–M2–M2^{iv}$		180
	$–M1^{iii}$	2.776(2)			

[a] Symmetry codes: (i) $x, y, 1 + z$; (ii) $-x + y, -x, z$; (iii) $1 - x + y, 1 - x, z$; (iv) $x, y, -1 + z$.

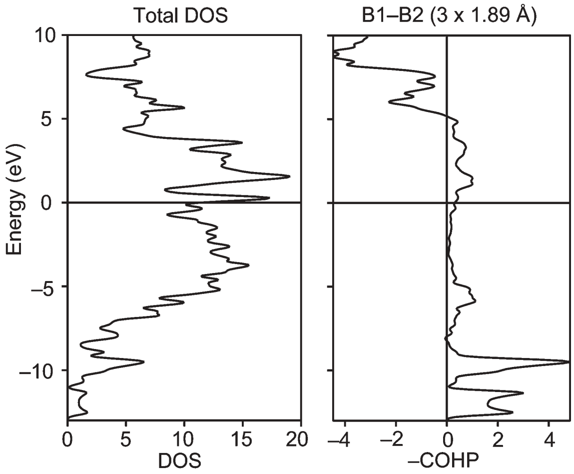

Fig. 4 Theoretical density-of-states (DOS) of $Ti_{1.6}Os_{1.4}RuB_2$ and COHP bonding analysis of the B1–B2 interactions; the Fermi level has been set to the energy zero.

interactions up to the Fermi level (Fig. 4, right), with an energy integral (ICOHP) of approximately 900 kJ mol^{-1} for the entire B_4 unit with three B–B bonds. The analysis further shows that the latter unit could host even more electron density since there are virtual bonding levels seen in the conduction band. Because of the finite density-of-states (DOS) at the Fermi level (Fig. 4, left), the phase is predicted to be a metal, as expected, and the slightly lowered DOS just above the Fermi edge also indicates that this very structure type might accommodate additional electrons.

The structure of $Ti_{1.6}Os_{1.4}RuB_2$ contains the first trigonal planar B_4 unit ever seen in intermetallic phases and also holds one-dimensional M2 (mostly Ti) chains and one-dimensional strings of face-sharing empty tetrahedral and square pyramidal $(Ru/M1)_6$ clusters. The theoretical analysis confirms strong bonding interactions in the quasi-molecular B_4 unit.

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Notes and references

† Needle-shaped silvery single crystals of $Ti_{1.6}Os_{1.4}RuB_2$ were synthesized by arc-melting the elements in a water-cooled copper crucible under an Ar atmosphere using a tungsten tip as a second electrode. The starting materials, Ti (pieces, 99.9%, Degussa), Os (powder, 99.9%, Degussa), Ru (powder, 99.9%, Umicore) and B (pieces, 99.999%, Alfa Aesar), were weighted in the atomic ratios 1 Ti : 2 Os : 1 Ru : 2 B, pressed into pellets and arc-melted under argon until homogeneous melting was achieved; the Ar had been purified before over silica gel, molecular sieves, and Ti sponge (950 K). The reaction products were remelted several times to ensure good homogeneity of the samples. Weight losses during the melting process were negligible. 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 mainly shows intensities of the reported phase but also some weak intensities of the binary OsRu. The lattice parameters, however, were easily refined from these powder data using the program WinXpow (WinXpow, version 1.06, Stoe, Darmstadt, Germany, 1999).

‡ Crystal data: $Ti_{1.6}Os_{1.4}RuB_2$, M = 468.46, hexagonal, a = 8.8554(14) Å, c = 3.0336(7) Å, V = 206.02(7) $Å^3$, T = 293(2) K, space group $P\bar{6}2m$ (the highest-symmetry non-centric choice because of $|E^2 - 1|^2$ statistics), Z = 3; diffraction data collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å), empirical absorption correction μ = 74.941 mm^{-1} with SADABS,[20] 2271 reflections measured, 395 unique (R_{int} = 0.064). The final values for R_1 and wR_2 (all data) were 0.0402 and 0.0767 respectively. CCDC 612040. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b608903h. Crystal structure solution/refinement was done by means of SHELX programs.[21] The crystallographic data collected for two single crystals provided identical chemical compositions and were confirmed by EDX analyses on several crystals (1 : 1.56 : 1.44 for Ru : Ti : Os, 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[22] in its tight-binding representation[23] using the TB-LMTO-ASA 4.7 code.[24] The exchange–correlation contributions to the total energies were treated in the local-density approximation (LDA).[25] The chemical bonding situations were analyzed using the Crystal Orbital Hamilton Population (COHP) technique[26] as implemented in the TB-LMTO-ASA program package.

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