$Cs_7In_4Bi_6$: A Zintl Phase Tailored from the PbO-Type Layers of the Parent InBi Compound

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The title compound was made by fusion of stoichiometric mixture of the pure elements. The structure (triclinic, $P\bar{1}$, $Z = 4$, $a = 10.1851(4)$ Å, $b = 10.2318(7)$ Å, $c = 27.617(2)$ Å, $\alpha = 94.457(7)°$, $\beta = 91.462(6)°$, $\gamma = 90.214(6)°$) is based on In-centered tetrahedra of bismuth sharing edges to form folded chains. The latter are linked via In−In bonds in a rather complicated three-dimensional network. The structure can be explained as being carved out from the layered PbO-type structure of the parent group III−V compound of InBi. $Cs_7In_4Bi_6$ is a wide band-gap semiconductor according to EHMO calculations and magnetic measurements.

Introduction

The elements of group IV and the isoelectronic binaries of groups III−V and II−VI attract much interest due to their semiconducting properties. They provide a variety of band gaps and properties that can be modified by extrinsic doping, temperature, pressure, etc. Thus, at higher pressures silicon adopts the metal-like structure of β-tin while the metallic InBi becomes superconducting.[1] Alternatively the properties can be modified by changing the atomic charges, of course, and of particular interest to us has been the chemistry of the negatively charged early post-transition elements. Such oxidation states are obtained in compounds with the most electropositive elements in the periodic table, the alkali metals. Compounds such as A_4E_4 (A = alkali metal, E = group IV element), for example, contain tetrahedral E_4 "molecules" with a formal charge of 4−.[2] More recently, nine-atom deltahedral clusters of Si, Ge, Sn, and Pb with charge of 4− have been characterized in neat solids, i.e., solids made by direct synthesis from the elements.[3] All of these compounds are semiconductors with a variety of band gaps.

Our attention has been also drawn toward mixtures of elements, not just one element, that are similarly modified by alkali metals. Such compounds, for example, are the recently synthesized Cs_6Ge_8Zn with dimers of Ge_4 tetrahedra connected through faces by Zn, K_6Pb_8Cd with oligomers of four Pb_4 tetrahedra joined through faces by cadmium, and Cs_6Pb_8Hg with dimers of Pb_4 tetrahedra connected through edges by Hg.[4] Here we report on the synthesis and structure of $Cs_7In_4Bi_6$ which can be considered as derived from the group III−V parent compound InBi by reduction of the latter. It is a remarkable example of how upon such reduction a structure is rearranged and tailored effortlessly to a new one that can accommodate the additional cations (and charges) without excessive "cutting and pasting".

Experimental Section

All manipulations were performed in a glovebox filled with purified N_2 (moisture content less than 0.1 ppm). Mixture of the elements (all from Alfa-Aesar, ≥99.9% pure) with stoichiometry $Cs_5In_5Bi_4$ was sealed in a niobium container by arc-welding, the latter was jacketed in a fused silica ampule which was then sealed after evacuation. The assembly was heated at 900 °C for 1 day and cooled to room temperature at a rate of 50 °C/h. This particular stoichiometry was chosen in an attempt to make a deltahedral cluster $[In_5Bi_4]^{5-}$ that is isoelectronic and isostructural with the known $E_9{}^{4-}$ (E = group 14 element).[3] The product contained traces of $CsBi_2$ and unreacted Bi. After the structure and stoichiometry were determined, a reaction loaded as $Cs_7In_4Bi_6$ produced the compound in high yield and very good crystallinity when heated at 550 °C for longer time (2 weeks) and cooled with a rate of 10 °C/h. The reaction product was contaminated with traces of unidentified amorphous phase which was easily separated under microscope in the glovebox.

Single crystals of the compound were obtained from the reaction loaded as $Cs_5In_5Bi_4$. They were mounted in glass capillaries (subsequently flame-sealed at both ends in order to protect the crystals from oxygen and moisture) and checked for singularity. Data from one of them (gray-metallic, irregular shape, 0.3 × 0.2 × 0.2 mm) were collected on an Enraf-Nonius CAD4 single-crystal diffractometer with monochromated Mo Kα radiation at 21 °C ($\omega-2\theta$ scans, $2\theta_{max} = 50°$, a hemisphere). The 10 041 reflections were corrected for Lorentz and polarization effects, and for absorption with the aid of the average of three ψ scans (and later Xabs). The structure was solved by direct methods in $P\bar{1}$, and was refined on F^2 with the aid of the SHELXTL V5.0 package. The final residual indices are somewhat on the high side mainly due to problems stemming from strong and anisotropic absorption. After all the compound is made of very heavy elements only (Bi, Cs, and In are with atomic numbers 83, 55, and 49, respectively). Details of the data collection and structure refinements are given in Table 1, while positional and equivalent isotropic displacement parameters and important distances are listed in Tables 2 and 3, respectively. Qualitative microprobe analysis performed on the same single crystal confirmed the presence of Cs, In, and Bi only.

The magnetization of 14 mg of compound (only crystals carefully picked under microscope) was measured on a Quantum Design MPMS-SQUID magnetometer at a field of 3 T in the temperature range 10−

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Table 1. Selected Data Collection and Refinement Parameters for $Cs_7In_4Bi_6$

empirical formula	$Cs_7In_4Bi_6$
fw	2643.53
space group, Z	$P\bar{1}$ (No. 2), 4
unit cell params	$a = 10.1851(4)$ Å $b = 10.2318(7)$ Å $c = 27.617(2)$ Å $\alpha = 94.457(7)°$ $\beta = 91.462(6)°$ $\gamma = 90.214(6)°$ $V = 2868.3(3)$ Å^3
radiation, λ	Mo Kα, 0.710 73 Å
temp	20 °C
abs coeff	485.5 cm^{-1}
density (calcd)	6.122 g/cm^3
R indices ($I > 2\sigma_I$)^a	R1 = 7.48%, wR2 = 19.17%
R indices (all data)	R1 = 9.82%, wR2 = 36.06%

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2F_o^2 + (0.1406P)^2 + 306.6713P]$, $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for $Cs_7In_4Bi_6$

atom	x	y	z	U(eq)
Bi1	0.3119(1)	0.7808(1)	0.47190(4)	0.0163(3)
Bi2	−0.1379(1)	0.6457(1)	0.46633(5)	0.0175(3)
Bi3	0.4801(1)	0.7101(1)	0.30927(5)	0.0163(3)
Bi4	0.7791(1)	0.5378(1)	0.19013(5)	0.0182(3)
Bi5	0.1666(1)	0.4485(1)	0.35104(5)	0.0168(3)
Bi6	0.4888(1)	0.8374(1)	0.14584(5)	0.0180(3)
Bi7	0.9631(1)	0.9754(1)	0.14206(5)	0.0198(3)
Bi8	0.0254(1)	0.9240(1)	0.35536(5)	0.0199(3)
Bi9	0.7868(1)	0.6838(1)	0.01992(5)	0.0175(3)
Bi10	0.3015(1)	0.3878(1)	0.18974(5)	0.0204(3)
Bi11	0.6116(1)	0.2266(1)	0.32283(5)	0.0223(3)
Bi12	−0.6559(1)	−0.1332(1)	0.96267(5)	0.0187(3)
In1	0.1349(2)	0.5393(2)	0.45484(8)	0.0175(5)
In2	0.7737(2)	0.7566(2)	0.12837(8)	0.0169(5)
In3	0.4172(2)	0.4125(2)	0.29331(9)	0.0186(5)
In4	0.5514(2)	0.8598(2)	0.04164(9)	0.0185(5)
In5	0.0348(2)	0.8927(2)	0.46235(8)	0.0167(5)
In6	0.4996(2)	0.6017(2)	0.20505(9)	0.0190(5)
In7	0.9030(2)	0.9626(2)	0.03594(8)	0.0171(5)
In8	0.2371(2)	0.7331(2)	0.36525(8)	0.0161(5)
Cs1	−0.1003(2)	0.2549(2)	0.41513(8)	0.0203(4)
Cs2	0.7165(2)	0.9001(2)	−0.08854(8)	0.0222(5)
Cs3	0.7479(2)	0.9073(2)	0.25662(8)	0.0224(5)
Cs4	0.5159(2)	0.4733(2)	0.07423(8)	0.0258(5)
Cs5	−0.3467(2)	0.9316(2)	0.41545(9)	0.0313(5)
Cs6	0.8181(2)	0.5718(2)	0.32934(8)	0.0289(5)
Cs7	0.3064(2)	0.1477(3)	0.4198(1)	0.0361(6)
Cs8	0.1187(2)	0.6964(2)	0.23132(9)	0.0317(5)
Cs9	0.5220(2)	0.4869(2)	0.42693(8)	0.0268(5)
Cs10	0.9583(2)	0.3418(3)	0.0886(1)	0.0363(6)
Cs11	0.1684(2)	0.6940(3)	0.0720(1)	0.0415(7)
Cs12	0.3193(2)	0.0321(3)	0.2608(1)	0.0381(6)
Cs13	0.6275(2)	0.1942(2)	0.17790(9)	0.0280(5)
Cs14	0.9809(3)	0.2536(3)	0.2506(1)	0.0370(6)

Table 3. Important Distances (Å) in $Cs_7In_4Bi_6$

In 1−Bi1	3.052(3)	Bi 1−In1	3.052(3)
Bi2	3.003(3)	In5	3.063(3)
Bi2	2.993(3)	In8	3.025(3)
Bi5	2.970(3)	Bi 2−In1	3.003(3)
In 2−Bi4	2.918(3)	In1	2.993(3)
Bi6	3.060(3)	In5	3.085(3)
Bi7	2.944(3)	Bi 3−In3	3.105(3)
Bi9	3.036(3)	In6	3.015(3)
In 3−Bi3	3.105(3)	In8	2.952(3)
Bi5	3.052(3)	Bi 4−In2	2.918(3)
Bi10	3.057(3)	In6	2.956(3)
Bi11	2.896(3)	Bi 5−In1	2.970(3)
In 4−Bi6	2.989(3)	In3	3.052(3)
Bi9	3.047(3)	In8	2.990(3)
Bi12	3.002(3)	Bi 6−In2	3.060(3)
Bi12	3.002(3)	In4	2.989(3)
In 5−Bi1	3.063(3)	In6	3.018(3)
Bi2	3.085(3)	Bi 7−In2	2.944(3)
Bi8	2.996(3)	In7	2.971(3)
In5	3.004(5)	Bi 8−In5	2.996(3)
In 6−Bi3	3.015(3)	In8	2.936(3)
Bi4	2.956(3)	Bi 9−In2	3.036(3)
Bi6	3.018(3)	In4	3.047(3)
Bi10	2.970(3)	In7	3.079(3)
In 7−Bi7	2.971(3)	Bi 10−In3	3.057(3)
Bi9	3.079(3)	In6	2.970(3)
Bi 2	3.067(3)	Bi 11−In3	2.896(3)
In7	2.976(4)	Bi 12−In4	3.002(3)
In 8−Bi1	3.025(3)	In4	3.002(3)
Bi3	2.952(3)	In7	3.067(3)
Bi5	2.990(3)		
Bi8	2.936(3)		

300 K. For the measurements the sample was contained in a special holder designed for air-sensitive compounds. This holder is made of 3 × 5 × 160 mm (ID × OD × length) tubing and two half-length pieces of tightly fitting rods, all made of fused silica. One of the rods is inserted all the way into the tubing and the ends of tubing and rod are sealed together. The sample is then loaded from the other end of the tube (inside the glovebox), the other piece of rod is inserted, and the second end is sealed as well. The raw data were corrected for the susceptibility of the container and the ion-core diamagnetism of $7Cs^+$, $4In^{3+}$, and $6Bi^{5+}$. The resulting temperature independent magnetic susceptibility is negative and within the range $(-3.34$ to $-3.40) \times 10^{-4}$ emu/mol.

Results and Discussion

The structure of $Cs_7In_4Bi_6$ is fairly complicated, especially at a first look (Figure 1). Six of the eight unique indium atoms (inner indium − In_i) are tetrahedrally coordinated by the twelve unique bismuth atoms (Figure 2). The latter are one-, two-, and three-bonded to indium with average distances of 2.896, 2.968, and 3.029 Å, respectively (Table 3). No Bi−Bi bonding exists but, quite surprisingly, there are In−In bonds involving two indium atoms (outer indium, In_o) despite the fact that the compound is bismuth-rich. Many pnictide-rich compounds in the general system of alkali or alkaline-earth metal combined with group III and V elements show rather pnictide−pnictide bonding.[5] $Cs_7In_4Bi_6$ seems to be the first pnictide-rich compound (atomic ratio of pnictide to group III element larger than 1) with bonds between group III atoms without the presence of bonds between the pnictide atoms. The only other similar example is found in $Na_2Ga_3Sb_3$ with Ga−Ga bonds and no Sb−Sb bonds,[6] but clearly this compound is not pnictide-rich. The structure of $Cs_7In_4Bi_6$ can be described as built of chains of In_i-centered tetrahedra of bismuth that share two of the six available edges. The complications in the structure are primarily due to the different sharing modes of the tetrahedra, trans and cis. This alone causes the chains to twist and turn throughout space, and results in the fairly long c axis, 27.617(2) Å. The symmetry is also very low, triclinic, and this is quite unusual for extended structures. Most of the reported compounds in these systems, alkali-metal−group 13−group 15, are orthorhombic or mono-

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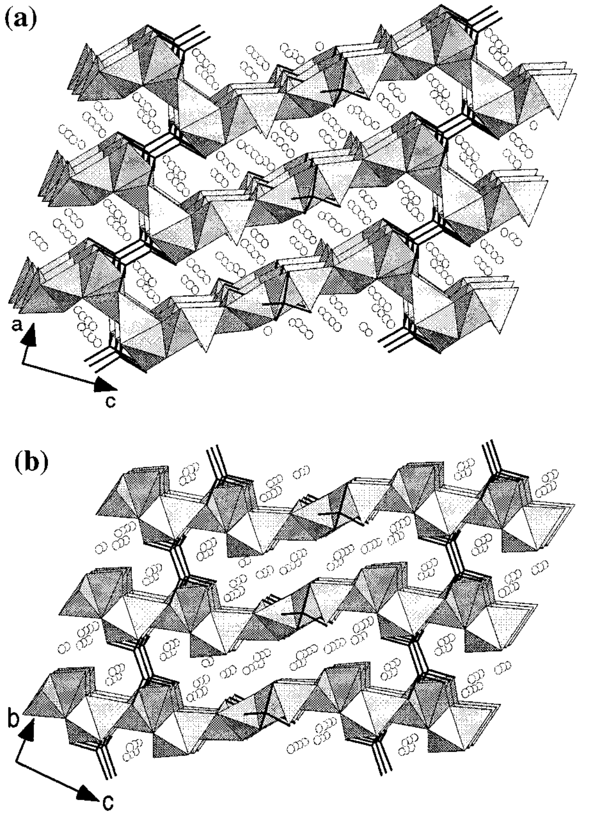

Figure 1. Two polyhedral views of the triclinic structure of $Cs_7In_4Bi_6$: (a) approximately along *b*; (b) approximately along *a*. Shown are the Bi_4 tetrahedra centered by In (inner indium, In_i) and the In−In bonds (outer indium, In_o) connecting the chains. The empty circles represent the cesium countercations that fill the openings between the chains.

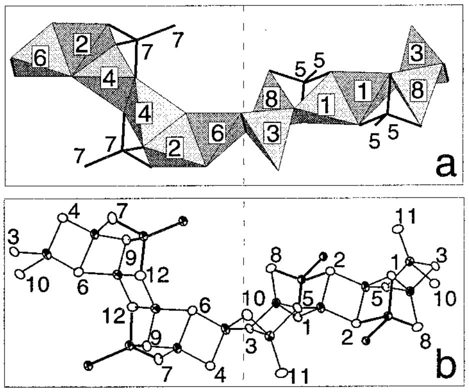

Figure 2. Polyhedral (a) and ORTEP views (b) of the repeating unit in $Cs_7In_4Bi_6$ (thermal ellipsoids at the 93% level) along a direction similar to that in Figure 1b. The indium and bismuth atoms are numbered in a and b, respectively. Important dihedral angles between tetrahedral faces: 115.86(3), 66.94(3), 112.92(3), 67.68(3), and 73.80(3)° for the pairs of tetrahedra centered by indium atoms 6-2, 2-4, 3-8, 8-1, and 3-6, respectively. The broken vertical line separates the two equivalent (but crystallographically different) fragments of the repeating unit (see text).

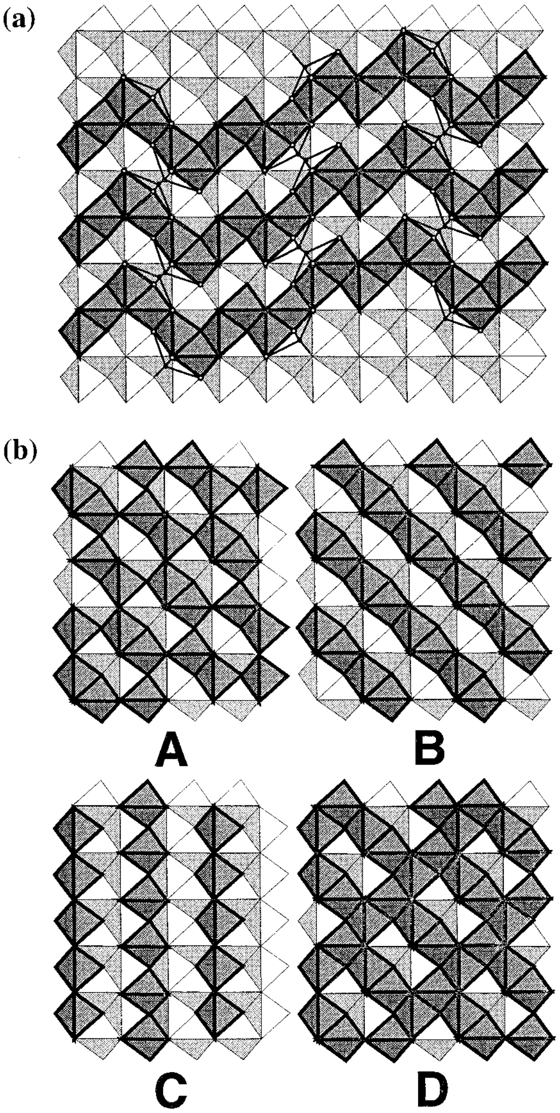

Figure 3. (a) Shown is how the chains in $Cs_7In_4Bi_6$ can be carved out from a layer of InBi. The layer is made of In-centered tetrahedra of Bi that share four of the six edges. Also shown are the In−In bonds between the outer indium atoms (In_o) that connect the chains. (b) Other alkali or alkaline-earth metal−triel (Tr)−pnictide (Pn) structures can be derived from a layer of "InBi". Shown are the structures of **A**, $K_2NaInSb_2$; **B**, $K_2Na(In\ or\ Ga)(As\ or\ P)_2$, K_3InP_2, Na_3AlAs_2; **C**, $Ca_3(Al\ or\ Ga)As_3$, Ca_3AlSb_3, Sr_3InP_3, Sr_3GaSb_3; **D**, $K_3In_2As_3$.

clinic regardless of the bonding between the tetrahedra, i.e., regardless of whether edges or corners are shared.

Further complications in $Cs_7In_4Bi_6$ come from the way the chains are connected to each other. This is done via two sets of In_o−In_o bonds, 3.004(5) and 2.976(4) Å, that are nearly perpendicular to the chains as well as to each other (Figure 2). Each In_o is also bonded to three bismuth atoms of two neighboring tetrahedra sharing an edge. As a result of this and in order for the bismuth atoms to be approximately equidistant from the corresponding In_o, the tetrahedra swivel around the pivoting common edge. This leads to much smaller dihedral angles between the tetrahedral faces than the ideal 109.5°. The foldings are clearly visible in the polyhedral view of the basic repeating unit of the chains shown in Figure 2a. The sequence of folded and "straight" tetrahedra as well as *trans*- and *cis*-edge sharing gives the chains their unusual shape. The repeating unit can be written $(TCT\mathit{i}TCTCCT\mathit{i}TCC)_n$ where T and C represent *trans*- and *cis*-tetrahedra, respectively, and *i* indicates an inversion center. It is interesting to note that the two fragments of the repeating unit (left and right in Figure 2) are with virtually identical connectivity but are twisted at about 90° with respect to each other. This semi-orthogonality of the fragments as well as the corresponding two sets of In_o−In_o bonds makes the structure three-dimensional.

Perhaps the most interesting feature in this compound is its relation to the structure of the parent group III−V compound of InBi. The latter is of the layered type with layers built of tetrahedra sharing four of the six edges.[7] This is the PbO-type structure (also known as LiOH-type), and InBi is the only group III−V compound that belongs to this structural type (the others are with the zinc blende structure).[7,8] Recently it has been shown that under high pressure the layers of InBi get much closer and the compound becomes superconducting.[1] Interestingly, the structure of the new compound $Cs_7In_4Bi_6$ can be derived from the same layers of InBi. First, the chains are carved out of the layers as shown in Figure 3a. In essence, this is done by removing half of the indium atoms from the bismuth tetrahedra. This leads to an In:Bi molar ratio of 1:2 and to a charge imbalance of 3− per removed indium atom, i.e., $InBi_2^{3-}$ or $In_6Bi_{12}^{18-}$. The chains resulting from this "process" are flat since they are confined within the two-dimensional layers. Next, the two outer indium atoms are added and the formula becomes $In_8Bi_{12}^{12-}$. These atoms bond to some of the neighboring tetrahedra and form connections between the chains. Since each of the interchain In−In bonds requires two additional electrons, the final formula of the anionic part of the structure can be written as $In_8Bi_{12}^{14-}$. This essentially defines the formula of the compound, $Cs_{14}In_8Bi_{12}$ or $Cs_7In_4Bi_6$. The local folding of the tetrahedra due to the bonding to outer indium causes the chains to coil and roll, and sculptures them into the final three-dimensional product. After discovering this relatively simple way to represent the structure, we found that the same approach works also very well for other compounds of group III−V with alkali or alkaline-earth metals. Figure 3b shows how other known structural types can be carved out from the same PbO-type layer by using "cookie-cutters" with different shapes. Thus in $(K_2Na)InSb_2$,[9] for example, every other pair of tetrahedra in an imaginary "InSb" layer is empty (**A** in Figure 3b). Such representation makes the otherwise complex-looking structure look quite understandable. For five other compounds with the same stoichiometry, A_3TrPn_2 (Tr = triel and Pn = pnictide are group III and V atoms, respectively), vacant are alternating chains of tetrahedra (**B** in Figure 3b).[10] The structure of the alkaline-earth−III−V compounds of stoichiometry $(AE)_3TrPn_3$ is relatively simple to describe without this approach as chains of corner-sharing tetrahedra.[11] Nevertheless, the same approach of a carved out layer is applicable as well (**C** in Figure 3b). The structure of $K_3In_2As_3$ looks quite tangled when viewed alone.[12] Nonetheless, it is easily explained as a layer of "InAs" where every third pair of tetrahedra is empty (**D** in Figure 3b). In addition to these extended structures the more molecular structure of $(AE)_3TrPn_3$ containing dimers of edge-sharing tetrahedra can be also cut out of such layers.[13] Perhaps there are other known as well as "yet to be discovered" structures that could be explained in the same systematic manner thus relating seemingly complicated and unrelated structures.[14] This general approach is of course nothing new in the structural solid-state chemistry. It is very reminiscent to the way octahedral structures such as rutile, PbO_2, and a large variety of shear structures of Mo, V, and Nb oxides are derived from the NaCl or ReO_3 structures.[8] The approach has been heavily used in describing complicated structures since it makes them indeed understandable. Here we have pointed at the parent structure of yet another class of structures that seemed to be totally unrelated before.

Extended Hückel calculations of the anionic part of $Cs_7In_4Bi_6$ show a relatively large band gap of more than 5 eV. This is not surprising since the compound is electronically balanced, i.e., the numbers of bonding and provided electrons are equal, and involves elements with quite different electronegativities. On the basis of the simple octet rule considerations, the electrons can be counted as follows. Of the 12 unique Bi atoms one is one-bonded and therefore carries a formal charge of −2, four are two-bonded and the charge is −1 per atom, and the remaining atoms are three-bonded with a zero negative charge. All eight indium atoms are four-bonded and therefore carry a charge of −1 each. This gives total of 14 negative charges, and they are balanced by the fourteen Cs cations. The temperature-independent and negative magnetic susceptibility of the compound is consistent with its "salt-like" nature.

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Supporting Information Available: An X-ray crystallographic file, in the CIF format, for the structure determination of $Cs_7In_4Bi_6$ is available free of charge via the Internet at http://pubs.acs.org.

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(14) Work is in progress on the structure of yet another compound in the system A−Tr−Pn which can be described as being "cut-out" of the InBi layer as well. It contains simple helical chains of edge-sharing tetrahedra.