

Synthesis and Characterization of Cs₅In₃As₄ with a Structure of Two Coexisting “Polymorphic” Forms of Different Dimensionality

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Received June 18, 2001

The title compound was made by fusion of a stoichiometric mixture of the pure elements at 500 °C. The structure (monoclinic, $P2_1/c$, $Z = 8$, $a = 17.037(6)$, $b = 12.253(1)$, $c = 18.105(4)$ Å, $\beta = 117.24(2)^\circ$) is made of alternating one- and two-dimensional sections with the same composition of Cs₅In₃As₄, and can be considered as two coexisting polymorphic forms of the same compound. The chains and layers in these sections are made of repeating semicubane motifs of [In₃As₄]⁵⁻ that are connected to each other by In–As bonds in the chains, and by both In–As and In–In bonds in the layers. According to magnetic measurement and EHMO calculations, Cs₅In₃As₄ is a closed-shell compound that fulfills the Zintl concept.

Introduction

The structural chemistry of the heteroatomic anions of groups 13 (Tr from Triels = Al, Ga, In, Tl) and 15 (Pn from Pnictogens = P, As, Sb, Bi), [Tr_{*m*}Pn_{*n*}]^{*q-*}, is quite rich.¹ Already characterized are a number of such species with different compositions, charges, and connectivities. Most of them are built of Tr-centered tetrahedra of Pn₄ which share edges and/or corners to build structures of all dimensionalities. Some of them, such as K₁₀In₅Sb₉, Ba₇Ga₄Sb₉, and A₂Tr₂Pn₃, exhibit Pn–Pn bonds,¹ but until recently, only one compound with Tr–Tr bonds was known, Na₂Ga₃Sb₃.² However, this latter group has grown substantially lately, and now includes Cs₇In₄Bi₆,³ K₆Tl₂Sb₃, and the isostructural K₆Tl₂Bi₃,⁴ (K or Rb)₇In₄Bi₆ which differ structurally from Cs₇In₄Bi₆ despite the same stoichiometry,⁵ K₁₁In₆Bi₉,⁵ and BaGa₂Sb₂.⁶ Here we report the synthesis and quite remarkable structure of yet another compound with Tr–Tr bonds, Cs₅In₃As₄. The anionic part of the structure contains both chains and layers of interconnected defect cubanes of three indium and four arsenic atoms. Furthermore, even more unusual, both the layers and the chains have exactly the same overall composition of [In₃As₄]⁵⁻, and the compound can be considered as made of two coexisting polymorphic forms of itself.

Experimental Section

Synthesis. All manipulations were performed inside a nitrogen-filled glovebox with moisture level below 1 ppm. The starting materials Cs

(99.95%, from Acros), In (99.9%, from Alfa-Aesar), and As (99.5%, from Alfa-Aesar) were used as received. Mixtures of them were loaded in niobium containers that were then sealed by arc welding under argon. The containers were enclosed in fused-silica ampules that were flame sealed under vacuum. These assemblies were heated at 500 °C for 4 days and were then cooled to room temperature at a rate of 5 °C per hour. Initially, the compound was synthesized from a reaction intended to produce heteroatomic deltahedral clusters [In₄As₅]³⁻ isostructural and isoelectronic with the known nine-atom clusters of group 14, E₉⁴⁻.⁷ Later, after the stoichiometry was established from the structure determination, Cs₅In₃As₄ was made in high yield from a mixture with the corresponding composition. The synthesis can be successfully carried out at temperatures up to 800 °C, above which arsenic reacts with the container. The compound is highly air- and moisture-sensitive and crystallizes as dark-gray to black bars or plates with some coal-like luster.

Structure Determination. Crystals of the compound were mounted in glass capillaries (inside a drybox) and checked for singularity on an Enraf-Nonius CAD4 single-crystal diffractometer (Mo K α radiation, $\lambda = 0.71073$ Å). A quadrant of a sphere of data was collected on the best crystal (bar-like, $0.2 \times 0.04 \times 0.04$ mm) at room temperature ($2\theta_{\max} = 50^\circ$, $\omega - 2\theta$ scans). The structure was solved in the monoclinic space group $P2_1/c$ and refined (on F^2) with the aid of the SHELXTL-V5.1 software package. Empirical absorption correction was applied using the Xabs program. Details of the data collection and refinement are given in Table 1, while the final positional and equivalent isotropic displacement parameters and important distances are listed in Tables 2 and 3, respectively.

Magnetic Measurements. The magnetization of 43 mg of Cs₅In₃As₄ was measured on a Quantum Design MPMS SQUID magnetometer at a field of 3 T over the temperature range 10–250 K. The sample was sealed in a fused-silica tubing (I.D. = 3 mm) between two tightly fitting rods of the same material. The results showed negative and temperature-independent magnetic susceptibility varying within $-(0.7-1.0) \times 10^{-4}$ emu mol⁻¹ (after correction for the holder).

Extended Hückel Calculations. Calculations within the tight binding approximation were carried out for the anionic parts of the structure on the basis of 100 *k* points using the extended Hückel method.⁸ Employed were the following atomic orbital parameters H_{ii}

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Table 1. Selected Data Collection and Refinement Parameters for Cs₅In₃As₄

formula	Cs ₅ In ₃ As ₄
fw	1308.69
space group, <i>Z</i>	<i>P</i> 2 ₁ / <i>c</i> , 8
lattice parameters	<i>a</i> = 17.037(6) Å <i>b</i> = 12.253(1) Å <i>c</i> = 18.105(4) Å <i>β</i> = 117.24(2)° <i>V</i> = 3360.1(1) Å ³
radiation, <i>λ</i>	Mo Kα, 0.710 73 Å
temp	20 °C
abs coeff	225.40 cm ⁻¹
density (calcd)	5.175 g/cm ³
<i>R</i> indices (<i>I</i> > 2σ) ^a	<i>R</i> 1 = 4.04%, w <i>R</i> 2 = 11.22%
<i>R</i> indices (all data)	<i>R</i> 1 = 7.98%, w <i>R</i> 2 = 14.59%

^a *R*1 = $\sum ||F_o| - |F_c|| / \sum |F_o|$ and w*R*2 = $\{[\sum w(F_o)^2 - (F_c)^2] / [\sum w(F_o)^2]\}^{1/2}$, for $F_o^2 > 2\sigma(F_o^2)$ and $w = [\sigma^2(F_o)^2 + (0.1107P)^2 + 120.7544P]^{-1}$, where $P = [(F_o)^2 + 2(F_c)^2]/3$.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for Cs₅In₃As₄

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
In1	0.49455(7)	0.1245(1)	0.05163(7)	0.0127(3)
In2	0.46951(8)	0.7675(1)	0.27854(8)	0.0135(3)
In3	0.52342(8)	0.9771(1)	0.22494(8)	0.0136(3)
In4	-0.00652(8)	0.7464(1)	-0.20013(8)	0.0130(3)
In5	0.00391(8)	0.9935(1)	0.20104(8)	0.0135(3)
In6	0.08593(8)	0.3754(1)	-0.10236(8)	0.0153(3)
As1	0.3896(1)	0.1272(1)	0.1320(1)	0.0135(4)
As2	0.4218(1)	0.6844(1)	-0.0996(1)	0.0143(4)
As3	0.5902(1)	0.9375(1)	0.1103(1)	0.0132(4)
As4	0.3598(1)	0.6201(1)	0.1643(1)	0.0157(4)
As5	0.1519(1)	0.1234(1)	0.2728(1)	0.0149(4)
As6	-0.0441(1)	0.5424(1)	-0.1766(1)	0.0141(4)
As7	0.1066(1)	0.8776(1)	-0.0774(1)	0.0152(4)
As8	-0.0445(1)	0.2096(1)	-0.1792(1)	0.0136(4)
Cs1	0.10028(8)	0.6281(1)	0.03941(7)	0.0236(3)
Cs2	0.08293(8)	0.1240(1)	0.03622(7)	0.0264(3)
Cs3	0.56229(9)	0.6336(1)	0.13809(8)	0.0314(3)
Cs4	0.35530(8)	0.3980(1)	0.03044(8)	0.0304(3)
Cs5	0.21641(7)	0.1340(1)	-0.09427(7)	0.0208(3)
Cs6	0.35164(7)	0.8540(1)	0.03547(7)	0.0203(3)
Cs7	0.20982(7)	0.6202(1)	-0.10380(8)	0.0229(3)
Cs8	0.23607(7)	0.8748(1)	-0.21214(7)	0.0213(3)
Cs9	0.24962(8)	0.3383(1)	0.18479(8)	0.0286(3)
Cs10	0.25051(9)	0.9120(1)	0.18704(9)	0.0314(3)

and ζ_1 : As 4s -16.22 eV and 2.23, 4p -12.16 eV and 1.89; In 5s -12.60 eV and 1.90, 5p - 6.19 eV and 1.68.⁹

Results and Discussion

The structure of Cs₅In₃As₄ is unique in that it is made of alternating sections with different dimensionalities (Figure 1). Layers parallel to the *b,c* plane and isolated chains along the *b* axis are stacked on top of each other. The alternating portions containing these motifs, between the broken lines in Figure 1, are separated by the cesium cations, but some of the latter are also found within the sections between chains and within holes in the layers. The chains are well isolated from each other ($d_{\min} = 5.324(2)$ Å) and from the sheets ($d_{\min} = 5.484(2)$ Å). Remarkably, the composition of the chain section is exactly the same as that of the layer section, Cs₅In₃As₄. It is, therefore, like a structure made of alternating polymorphic forms of the same compound.

A closer look at the chains and layers (Figure 2) reveals that they are built of one and the same building block that is just connected to itself differently in the two fragments. The building

Table 3. Important Distances (Å) in Cs₅In₃As₄

layers			chains			
In1	As1	2.774(2)	In4	As5	2.726(2)	
	As2	2.671(2)		As6	2.663(2)	
	As3	2.716(2)		As7	2.704(2)	
In2	As3	2.730(2)	In5	As8	2.733(2)	
	As1	2.790(2)		As5	2.753(2)	
	As2	2.742(2)		As6	2.726(2)	
	As4	2.738(2)		As7	2.681(2)	
In3	In3	3.032(1)	As8	As8	2.661(2)	
	As1	2.811(2)		In6	As5	2.951(2)
	As3	2.829(2)			As6	2.859(2)
As4	As4	2.719(2)	As8	As8	2.858(2)	
	In2	3.032(1)		As5	In4	2.726(2)
	In1	2.774(2)			In5	2.753(2)
As1	In2	2.790(2)	In6	In6	2.951(2)	
	In3	2.811(2)		As6	In4	2.663(2)
	As2	2.671(2)			In5	2.726(2)
As2	In2	2.742(2)	In6	In6	2.859(2)	
	In1	2.716(2)		As7	In4	2.704(2)
As3	In1	2.730(2)	In5		In5	2.681(2)
	In3	2.829(2)		As8	In4	2.733(2)
	In2	2.738(2)			In5	2.661(2)
As4	In3	2.719(2)	In6	In6	2.858(2)	

block is a dimer of semicubanes, each made of three indium and four arsenic atoms (Figure 3), i.e., a cubane with one missing indium vertex. Defect cubanes of the same type are known in other compounds as well. For example, semicubanes of [Sn₃(S or Se)₄] are connected by corner sharing and/or with bridging atoms to form layers in Cs₈Sn₅S₁₂ and Cs₂Sn₅Se₇.¹⁰ The semicubanes of [In₃As₄] in Cs₅In₃As₄ are connected by two In-As bonds within each dimer. These are two equivalent In1-As3 bonds (related by an inversion center) of 2.716(2) Å in the layers, and the pairs of In4-As6 and In5-As8 (related by the 2₁ screw along *b*) with distances 2.663(2) and 2.661(2) Å in the chains. The chains, as it can be seen in Figure 2, can be also described simply as repeating monomers of semicubanes, since the dimers are connected to each other by the same pairs of In-As bonds as those forming the dimer itself. However, dimers are chosen in this description in order to underline the similarities with the layers. The dimers in the layers are connected to each other by In-In bonds. These bonds, 3.032(1) Å, are between the two indium atoms that are not involved in the intradimer bonding, In2 and In3 (Figures 2 and 3). This distance compares well with similar In-In distances observed in other compounds with the pnictogens, 3.004(5) and 2.976(4) Å in Cs₇In₄Bi₆,³ 2.85(2) Å in K₇In₄Bi₆,⁵ and 2.982(6) Å in K₁₁In₆Bi₉.⁵ The corresponding bond overlap population calculated by the extended Hückel method is substantial, 0.731. There are four such bonds per dimer and they provide the second dimension of the layers.

The In-As distances fall in three different categories depending upon the coordination of the indium atom. The shortest bonds are around indium atoms bonded to four arsenic atoms, i.e., In1, In4, and In5, and range from 2.661(2)-2.774(2) Å. They are quite typical for In-As distances and compare well with similar distances observed in K₈In₈Ge₅As₁₇ (2.591(9)-2.784(8) Å),¹¹ K₄In₄As₆ (2.611(1)-2.793(1) Å),¹² and Na₃InAs₂ (2.671(2)-2.774(2) Å).¹³ In the second category fall the distances around indium atoms bonded to three arsenic and one

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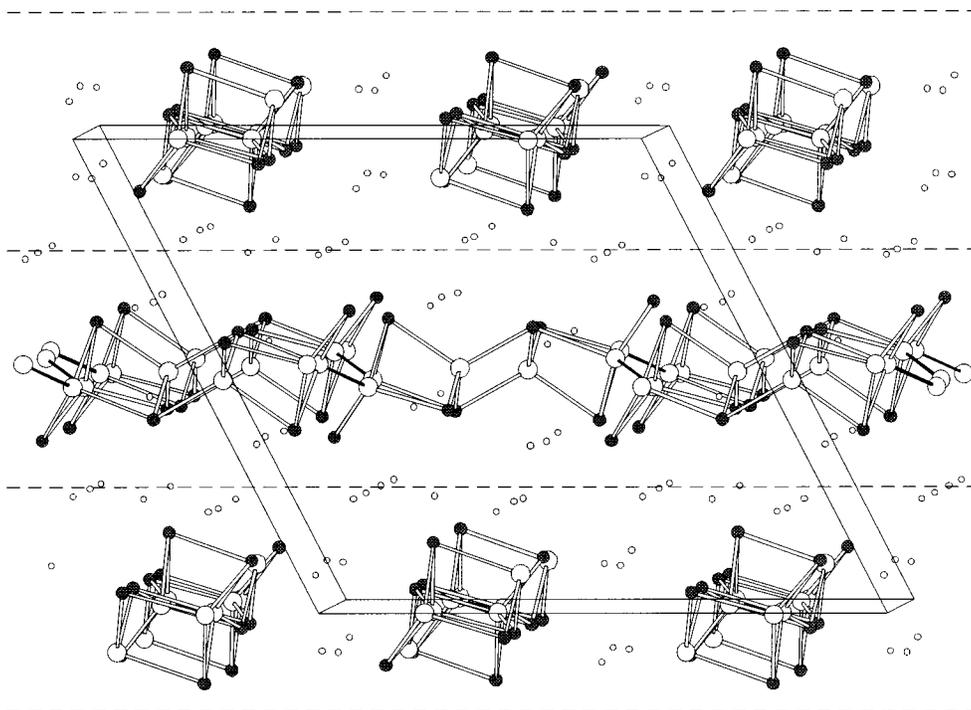


Figure 1. A view of the structure of $\text{Cs}_5\text{In}_3\text{As}_4$ along the b axis of the monoclinic cell (outlined, c is horizontal). The structure is made of sections (shown separated by broken lines) containing alternatingly chains and layers. The chains are along the b axis (the viewing direction), while the layers are parallel to the b, c plane. The bonds between In (large open circles) and As (filled circles) are shown as open, while the In–In bonds in the layers are shown as filled. The small, isolated circles are the cesium cations. The chain and layer sections are of the same composition, $\text{Cs}_5\text{In}_3\text{As}_4$, and the structure can be considered as a coexistence of two polymorphic forms with different dimensionality of the same compound.

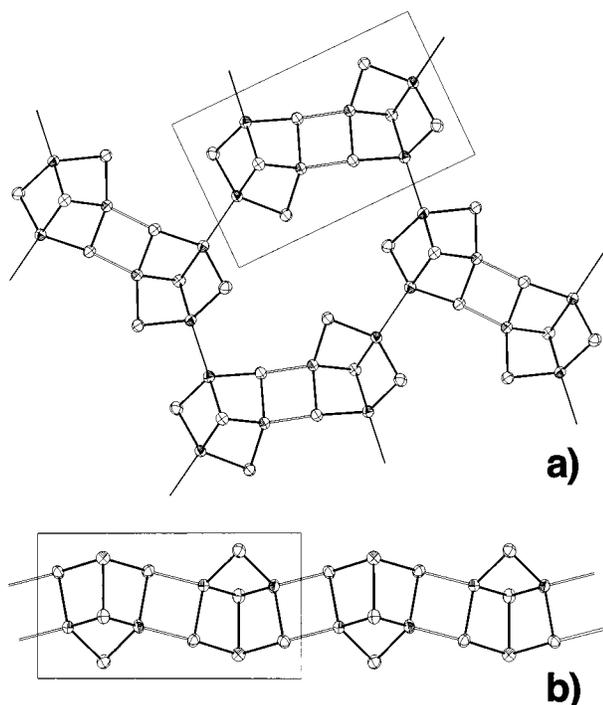


Figure 2. ORTEP drawings (thermal ellipsoids at the 90% probability level) of a) the layers and b) the chains in $\text{Cs}_5\text{In}_3\text{As}_4$ viewed normal to the b, c plane. Shown as boxed is the same building unit of the chains and the layers, dimers of semicubanes. Each semicubane is made of three indium and four arsenic atoms shown as full and crossed ellipsoids, respectively. The semicubanes are bonded by two In–As bonds (open) in each dimer. They are further connected to each other by the same pair of In–As bonds (open) in the chains, but with four In–In bonds (filled) in the layers.

indium atoms, i.e., In2 and In3, with distances from 2.719(2) to 2.829(2) Å. In the third category are the longest In–As bonds

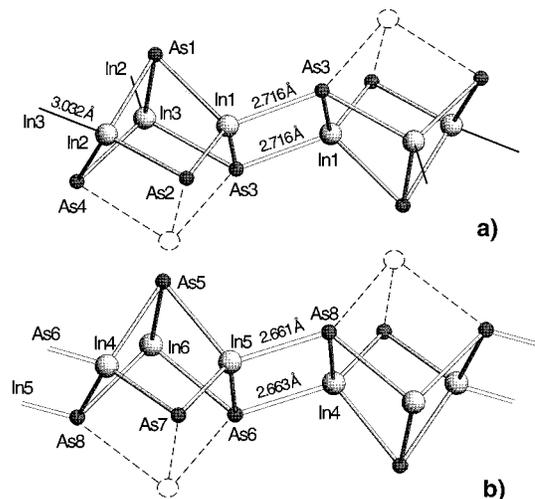


Figure 3. Closer side views (parallel to the plane of the layers and perpendicular to the b axis) of the bonding in a) the layers and b) the chains of $\text{Cs}_5\text{In}_3\text{As}_4$. The missing vertices of the semicubanes of $[\text{In}_3\text{As}_4]$ and the bonds to them are shown with broken lines.

found at the three-bonded indium atom, In6 in the chains, with distances of 2.858(2), 2.859(2), and 2.951(1) Å. This elongation is not surprising considering that this indium atom carries a lone pair of electrons which will strongly repel other atoms with lone pairs, such as its arsenic neighbors, As5, As6, and As8. The average calculated bond overlap population for these three bonds is the lowest, 0.262, compared with 0.380 for all other In–As bonds. The longer distances of the second category compared to those of the first category can be explained similarly. While the electrons of the indium atoms bonded to four arsenic atoms are substantially withdrawn toward the latter, they are not so much so for the indium atoms with In–In bonds due to the same electronegativity. As a result of this, the latter indium

atoms experience stronger repulsion from the lone pairs of the arsenic atoms. These same effects are observed in all other compounds with Tr–Tr bonds and/or a three-bonded Tr atom.^{2–5,14}

There are only two- and three-bonded arsenic atoms in the structure. Two of each kind are found in the layers, and there are one two-bonded and three three-bonded in the chains. The indium atoms are distributed as follows: three four-bonded in the layers and two four-bonded and one three-bonded in the chains. These bonding schemes, in turn, define the charges of the chains and the layers. Thus, in accordance with the octet rule, four- and three-bonded indium atoms carry formal charges of 1– and 2–, respectively, while three- and two-bonded arsenic atoms are neutral or 1–, respectively. When applied to the above-mentioned bonding schemes, the formulas become [(4b-In^{1–})₃(2b-As^{1–})₂(3b-As⁰)₂] for the layers and [(4b-In^{1–})₂(3b-In^{2–})(3b-As⁰)₃(2b-As^{1–})] for the chains. This, however, totals the same charge for both the layers and the chains, [In₃As₄]^{5–}, or expressed for the repeating unit of dimer of semicubanes, it is [In₆As₈].^{10–} Again, it is quite remarkable that one and the same building block of exactly the same composition, a dimer

of semicubanes, connects differently and forms extended motifs of different dimensionality while keeping the same charge and, correspondingly, the same requirement for counteranions. We have not been able to find any other compound that exhibits both chains and layers at the same time, let alone of the same composition and charge.

The results from the magnetic measurements, a negative temperature-independent magnetic susceptibility, and from the extended Hückel calculations, a band gap of more than 6 eV, confirm the closed-shell nature and composition of the compound. The density of states shows a broad band from –11 to –16 eV, which represents the In–As bonding interactions and the arsenic lone pairs. A band from –9.5 to –10.5 eV corresponds to the In–In bonds, while the highest filled band is at –8.0 to –8.5 and is due to the lone pairs at the three-bonded In6.

Acknowledgment. We thank the Petroleum Research Fund, administered by the ACS, for financial support of this research.

Supporting Information Available: An X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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