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KBa_2InAs_3 with Coexisting Monomers of $[In_2As_7]^{13-}$ and Their One-Dimensional Polymers

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The title compound was made by fusion of a stoichiometric mixture of the pure elements. The structure (orthorhombic, $Cmc2_1$, $Z = 16$, $a = 10.129(2)$ Å, $b = 25.208(4)$ Å, $c = 13.884(3)$ Å) is made of isolated units of $[In_2As_7]^{13-}$ and a polymer chain of $^1_\infty[In_2As_5]^{7-}$ made of the same units. According to magnetic measurement, KBa_2InAs_3 is a closed-shell compound, a Zintl phase.

Introduction

While complex systems based on alkali metal chalcogenides mixed with elements from various main and/or transition-metal groups have been studied very extensively,[1] similar systems based on alkali metal pnictides have not received nearly as much attention.[2] The former have shown great structural richness resulting mainly from the complexity of the mixtures that have been studied, usually quaternary and quintenary phases, and phases of even higher order. We have undertaken similar studies for the systems of alkali metal and arsenic where a third element or elements are added in order to modify the electronic requirements and, subsequently, the structural features. All initial signs suggest that, similarly to the chalcogenides (the selenides in particular), the arsenides will provide equally impressive structural richness, even for relatively simpler systems. In a recent article, we described one such compound, $Cs_5In_3As_4$, with the unique structure of coexisting chains and layers of the same composition and charge, $^1_\infty[In_3As_4]^{5-}$ and $^2_\infty[In_3As_4]^{5-}$.[3] This is almost as if two polymorphic forms of a compound coexist in one structure. We have now extended the complexity one step further and have studied the quaternary systems of alkali metal−alkaline earth metal−group 13−group 15, and we report here the synthesis and characterization of KBa_2InAs_3 which has coexisting monomers and their chainlike polymers. Mixing cations has proven to be a very effective approach in the exploratory studies of heavy main-group elements in their negative oxidation states.[4]

Experimental Section

Synthesis. All manipulations were performed inside a nitrogen-filled glovebox with moisture level below 1 ppm. The new compound was made from a mixture of the corresponding elements (all from Alfa-Aesar, used as received). The mixtures were loaded in niobium containers that were then sealed by arc welding under argon. These vessels were placed in fused-silica ampules that were then flame-sealed under vacuum. The initial synthesis was designed to produce an arsenic richer derivative of the cubane species $[In_3NbAs_4]$ with an exo-bonded arsenic at the Nb vertex found in $Cs_7NbIn_3As_5$,[5a] and therefore, the elements were in atomic ratio K/Ba/In/As = 4:3:3:8. The idea was to attach exo-bonded arsenic atoms to the three indium vertices of the cubane as well. The mixture was heated at 850 °C for 2 days and then slowly cooled to room temperature at a rate of 6 °C/h. In addition to KBa_2InAs_3, there was another phase that has not been identified yet. After the composition of the new compound was determined from the structure refinement and elemental analysis (see later), it was synthesized as a pure phase from the corresponding stoichiometric mixture (molar ratio K/Ba/In/As = 1:2:1:3) heated at a milder temperature of 500 °C and slowly cooled. The use of lower temperatures in the case of alkali metal−arsenic mixtures is necessary because, as we (and others) have found out, higher temperatures lead to ternary phases of alkali metal, arsenic, and niobium (or tantalum) from the container.[5] Thus, the yet unidentified phase of the initial reaction carried out at 850 °C is very likely a

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Table 1. Selected Data Collection and Refinement Parameters for KBa_2InAs_3

empirical formula	KBa_2InAs_3
fw	653.36
space group, Z	$Cmc2_1$, 16
unit cell parameters	$a = 10.129(2)$ Å
	$b = 25.208(5)$ Å
	$c = 13.884(3)$ Å
	$V = 3545.0(1)$ Å^3
radiation, λ	Mo Kα, 0.71073 Å
temp	20 °C
abs coeff	228.85 cm^{-1}
density (calcd)	4.897 g/cm^3
R indices ($I > 2\sigma_I$)[a]	R1 = 4.63%, wR2 = 11.77%
R indices (all data)	R1 = 5.71%, wR2 = 12.43%

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \{[\sum w[(F_o)^2 - (F_c)^2]^2]/[\sum w(F^2_o)^2]\}^{1/2}$ for $F_o^2 > 2\ \sigma(F_o^2)$; $w = [\sigma^2(F_o)^2 + (0.0821P)^2]^{-1}$ where $P = [(F_o)^2 + 2(F_c)^2]/3$.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement for KBa_2InAs_3

atom	site	x	y	z	U_{eq}	occupancy
In1	4a	0.5000	0.33452(7)	0.8013(1)	0.0156(4)	1.0
In2	4a	0.5000	0.29263(7)	0.5742(1)	0.0151(4)	1.0
In3	4a	0.0000	0.50605(7)	0.4579(1)	0.0133(4)	1.0
In4	4a	0.0000	0.54402(7)	0.6764(1)	0.0129(4)	1.0
As1	4a	0.0000	0.1999(1)	0.4822(2)	0.0200(7)	1.0
As2	4a	0.5000	0.4421(1)	0.7869(3)	0.0212(7)	1.0
As3	8b	0.2020(2)	0.20520(7)	0.1978(1)	0.0145(5)	1.0
As4	4a	0.5000	0.2145(1)	0.4523(3)	0.0267(8)	1.0
As5	4a	0.5000	0.3843(1)	0.4565(2)	0.0162(6)	1.0
As6	4a	0.5000	0.3597(1)	0.2809(2)	0.0207(7)	1.0
As7	4a	0.0000	0.3980(1)	0.4599(2)	0.0172(6)	1.0
As8	8b	0.7930(2)	0.54086(7)	0.5598(1)	0.0141(4)	1.0
As9	4a	0.0000	0.4569(1)	0.7787(2)	0.0160(7)	1.0
As10	4a	0.0000	0.3699(1)	0.2912(2)	0.0173(6)	1.0
Ba1/K1	8b	0.2208(2)	0.32921(8)	0.1226(2)	0.0237(7)	0.473(7)/0.527
Ba2/K2	4a	0.0000	0.2639(1)	0.6951(3)	0.026(1)	0.40(1)/0.60
Ba3/K3	4a	0.5000	0.4286(1)	0.0354(3)	0.034(1)	0.52(1)/0.48
Ba4/K4	8b	0.2821(1)	0.45818(4)	0.3271(1)	0.0191(5)	0.906(8)/0.094
Ba5/K5	8b	0.2962(3)	0.1251(1)	0.3810(2)	0.018(1)	0.115(7)/0.885
Ba6	8b	0.2306(1)	0.29033(4)	0.4028(1)	0.0220(3)	1.0
Ba7	8b	0.2365(1)	0.08259(5)	0.1226(1)	0.0194(3)	1.0

Nb-containing phase. The new compound is extremely air- and moisture-sensitive and crystallizes as dark gray thin plates with a coal-like luster.

X-ray Diffraction Studies. Selected crystals of the compound were mounted in glass capillaries (inside a drybox equipped with a microscope) and checked for singularity on an Enraf-Nonius CAD4 single-crystal diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å). An orthorhombic cell was identified, and a hemisphere of data was collected on the best crystal (platelike, $0.2 \times 0.1 \times 0.05$ mm^3) at room temperature ($2\theta_{max} = 50°$, $\omega-2\theta$ scans). The data were corrected for absorption with the aid of the average of 5 Ψ-scans at different θ angles. The structure was solved in the acentric orthorhombic space group $Cmc2_1$ and refined (on F^2) with the aid of the SHELXTL-V5.1 software package. 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.

The indium, arsenic, and cation positions were easily identified from the structure solution. However, it was not clear which of the seven independent cation positions were barium and which were potassium. Initially, barium was refined for all of them, and this led to quite large thermal parameters for five of the positions. When the occupancies of all seven positions were freed to vary, only those of the two barium atoms with normal thermal parameters, Ba6 and Ba7, refined as full (within a few σ), while the other five deviated significantly from unity (anywhere between 11σ and 120σ).

Table 3. Important Distances (Å) in KBa_2InAs_3

monomers		chains	
In1−As1	2.657(4)	In3−As7	2.657(4)
In1−As2	2.718(4)	In3−As8	2.677(2)
In1−As3	2.694(2)	In3−As8	2.677(2)
In1−As3	2.694(2)	In3−As9	2.725(4)
In2−As3	2.671(3)	In4−As7	2.616(3)
In2−As3	2.671(3)	In4−As8	2.650(3)
In2−As4	2.597(4)	In4−As8	2.650(3)
In2−As5	2.832(4)	In4−As10	2.692(4)
As5−As6	2.516(4)	As9−As10	2.447(4)

Consequently, the occupancies of Ba6 and Ba7 were fixed at full, while the other five were refined as fully occupied but with mixtures of potassium and barium where the ratios between the two elements were freed to vary. The possibility of having partially occupied sites by barium or by a mixture of barium and potassium was considered but was found unlikely because of the inability to make the compound without potassium and also the successful synthesis of the pure phase when using a mixture with the stoichiometric composition. Furthermore, the refined formula is consistent with an electronically balanced compound which was proven to be the case (see later), and the K/Ba ratio was confirmed by elemental analysis. The final refinement led to the formula $(K_{48-x}Ba_x)In_{16}As_{48}$ where $x = 31.63(2)$ which is very close to $K_{16}Ba_{32}In_{16}As_{48}$ (rationalized as KBa_2InAs_3).

Elemental Analysis. The K/Ba ratio was verified by elemental analysis carried out by ICP on a Perkin-Elmer Plasma 400 emission spectrometer (40 MHz free-running ICP generator and Ar-cooled coil). For that purpose, crystals of the compound were carefully selected under microscope and were dissolved in diluted acid. Also prepared were standards for the elements for four known concentrations. Multiple measurements for K and Ba gave an average atomic ratio of 1:1.978 for the two elements. Considering the accuracy of the ICP method, this ratio is in excellent agreement with the formula.

Magnetic Measurements. The magnetization of 30 mg of KBa_2InAs_3 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 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 −1.5 and -1.7×10^{-4} emu/mol (after correction for the holder and the ion core diamagnetism). This is consistent with diamagnetic, electronically balanced compound, a Zintl phase.

Results and Discussion

The structure of KBa_2InAs_3 is made of isolated units of $[In_2As_7]$ and polymeric chains made by polymerization of the same units (Figure 1). The isolated species (Figure 2) have the shape of 1-ethyl-1,3,3-trimethyl-cyclobutane with indium at the positions of the quaternary carbon atoms. Thus, diarsenic plays the role of the ethyl substituent while the three terminal and two bridging arsenic atoms are methyl- and methylene-like, respectively. A mirror plane that contains all atoms but As3 (Figure 2) passes through the species. This makes the four atoms In2, As4, As5, and As6 coplanar. Taking into account that As^-, As^{2-}, and In^- are isoelectronic with CH_2, CH_3, and C, respectively, we can easily determine the charge of the species as 13−, that is, $[In_2As_7]^{13-}$. (The "methyl" and "ethyl" substituents would have charges of 3− and 2−, respectively.) A more "inorganic" description of

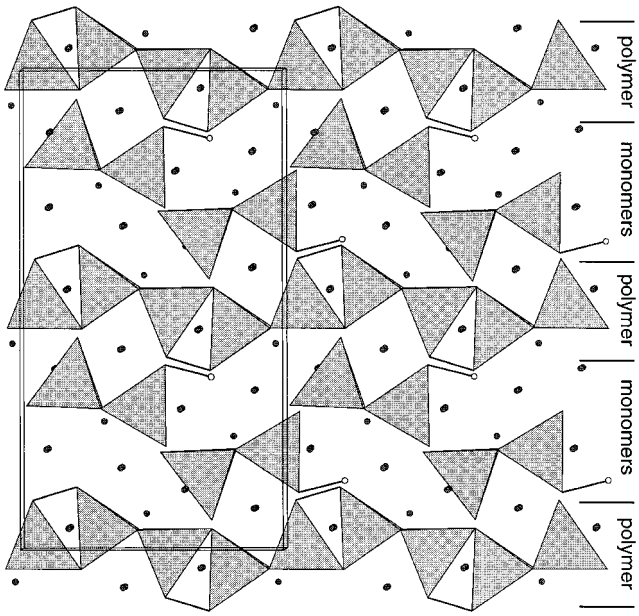

Figure 1. Polyhedral view of the structure of KBa_2InAs_3 along the *a* axis of the orthorhombic cell (outlined, *c* is horizontal). All tetrahedra are made of arsenic and are centered by indium atoms. The structure is made of sections containing alternatingly monomers and polymeric chains of the same monomers (labeled). The As−As bonds are shown both in the chains and the monomers. The isolated atoms are the cations in the structure.

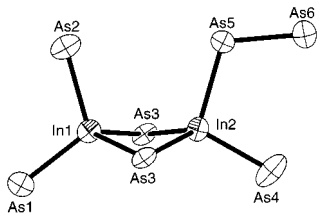

Figure 2. ORTEP drawing of the monomer of $[In_2As_7]^{13-}$ (thermal ellipsoids at the 95% probability level). All but the two As3 atoms are within a mirror plane which defines the planarity of the four atoms As4, In2, As5, and As6.

the structure of the species is to view it as made of two edge-sharing tetrahedra of arsenic that are centered by indium, and where an arsenic atom is exo-bonded to a corner of one of the tetrahedra, $[(As-As)As]In(\mu\text{-}As)_2In(As)_2$. Dimerization and polymerization of centered pnictide tetrahedra via common edges is quite a common feature in the pnictides of the less electronegative main-group elements.[2a] The four-membered ring formed by the bridging of the two tetrahedra is bent, a butterfly, with a dihedral angle of 39.99(6)° around the As3−As3 diagonal. The $[In_2As_7]^{13-}$ monomers are well separated from each other with $d_{min}(As-As) = 4.410(4)$ Å.

The chains in the structure are made of alternating five- and four-membered rings of $[In_2As_3]$ and $[In_2As_2]$, respectively (Figure 3), where the indium corners are shared between the rings. There is a mirror plane along the chain, and it contains the five-membered rings making them planar. As in the monomers, the four membered rings are made of two indium and two arsenic atoms (related by the mirror plane) and are bent (dihedral angle of 37.71(6)°). Most interestingly, one can easily recognize the described monomer as the repeating unit in the polymer (highlighted in Figure 3). Thus, the all-organic analogue of the chain would be a poly-1-ethyl-1,3,3-trimethyl-cyclobutane. The "polymerization" occurs at all terminal arsenic atoms making them 2-bonded and reducing by one the formal negative charge on each of them. Because of this sharing of the four arsenic atoms, the formula of the repeating unit is two arsenic atoms short from the formula of the monomer, $[In_2As_5]^{7-}$. The chains are well isolated from each other as well as from the monomers with $d_{min}(As-As)$ of 5.395(4) and 4.807(3) Å, respectively. The structure can therefore be described as containing both monomers and polymeric chains made of them. This is the second example that we have found where two fragments of different dimensionality coexist in the same structure. In the first one, $Cs_5In_3As_4$,[2] layers and chains with the same stoichiometry and charge, $[In_3As_4]^{5-}$, alternate in the structure in the same way as monomers and chains alternate in KBa_2InAs_3.

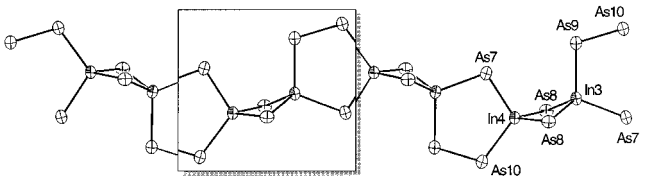

Figure 3. ORTEP drawing of part of the polymeric chain in KBa_2InAs_3 (thermal ellipsoids at the 95% probability level) made of the monomers shown in Figure 2. Highlighted is a motif of the chain which clearly has the same shape as the monomer. There is a mirror plane running along the chain that contains all but the As8 atoms. This makes perfectly planar the five-membered rings in the chain.

The In−As distances, 2.597(4)−2.832(4) Å, are quite typical for a four-bonded indium and compare well with the distances around similarly bonded indium in $Cs_5In_3As_4$ (2.661(2)−2.774(2) Å),[2] $K_4In_4As_6$ (2.611(1)−2.793(1) Å),[6] and Na_3InAs_2 (2.671(2)−2.774(2) Å).[7] They compare well also with the distances in molecular compounds with squarelike cores of $(InAs)_2$ such as $[Cl_2InAs^tBu_2]_2$, 2.652(1) Å; $[Ph_2InAs(SiMe_3)_2]_2$, 2.657(3)−2.679(2) Å; and $[Et_2InAs(SiMe_3)_2]_2$, 2.720(1) Å.[8] The As−As distance of 2.516(4) Å in the monomer is typical for single-bond distances such as 2.489(7) Å in the helical chains of KAs,[9] 2.511(4) and 2.563(3) Å in the dumbbells of $[As_2]^{4-}$ in $Na_2Sr_3As_4$,[10] as well as 2.52 Å in elemental gray arsenic.[11] The As−As distance of 2.447(4) Å in the polymer, on the other hand, is somewhat shorter than the single-bond distances given previously but is longer than 2.380(3) Å observed in the planar cyclic As_6^{4-} with one delocalized pair of π-electrons.[12] It compares rather well with the distances of the planar zigzag tetramer $As_4^{(4+\delta)-}$ in K_5As_4, 2.446(2) and 2.424(1) Å.[13] This tetramer exhibits a conjugated π-system with nearly two π-electrons distributed among the three bonds. The short

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As—As distance in the polymer and the planarity of the pentagonal ring suggest a similar explanation, that is, the existence of π-conjugation in the ring. This involves $p_\pi-d_\pi$ type π-interactions between empty d-orbitals of the indium atoms and filled p-orbitals of the arsenic atoms. The bonding resembles very closely the bonding in the well-known planar cyclophosphazenes such as squares of $(R_2P{=}N)_2$ and hexagons of $(R_2P{=}N)_3$ where the d- and p-orbitals are provided by the phosphorus and nitrogen atoms, respectively.[14] Calculations have shown that because of π-interactions between these orbitals and delocalization of valence electrons over three-atom P—N—P islands (Dewar's model[15]) the P—N distances are equal and shorter than single- but longer than double-bond distances.[16] Very similar is the situation within the five-membered arsenic−indium ring where six π-electrons are provided by the three arsenics. These six electrons delocalize on three bonding molecular orbitals formed by the three p-orbitals of the arsenic and the d-orbitals of the indium, exactly as in a cyclopentadienyl anion. Perhaps it is this delocalization that is responsible for the shorter As—As distance in the five-membered ring, 2.447(4) Å for As9—As10, compared to that of the monomer, 2.516(4) Å for As5—As6. We should note here that In2, As4, As5, and As6 of the monomer (Figure 2) are also coplanar and suggest similar $d_\pi-p_\pi$ interactions. However, in this geometry, the six π-electrons from the three arsenic atoms will occupy two bonding and one antibonding orbitals, thus giving the longer In2—As5 and As5—As6 distances. At the same time, the In2—As4 distance of 2.597(4) Å in the monomer is "elongated" to 2.657(4) Å for In3—As7 in the five-membered ring of the polymer. This can be easily explained by the change of the coordination of the arsenic atom from one- to two-bonded. Thus, the filled p_π-orbital of this arsenic atom interacts with one d_π-orbital in the monomer while the same orbital and number of electrons are shared with two such d_π-orbitals from the two neighboring indium atoms in the polymer.

The new compound KBa_2InAs_3 is electronically balanced, that is, the number of provided electrons by the cations equals the number of electrons needed for In−As and As−As bonding. This was confirmed by the magnetic measurements which showed negative and temperature-independent magnetic susceptibility. Its formula can be written as $(K^+)_4(Ba^{2+})_8\{[In_2As_7]^{13-}[In_2As_5]^{7-}\}$, and it can be called a Zintl phase. Structurally, the compound is one of the very few cases where structural fragments of different dimensionalities built of the same or similar motifs coexist in the structure.

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Supporting Information Available: 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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