Synthesis and characterization of the Zintl phase Na₄Ba₃As₆ with isolated As⁵⁻ anions

Franck Gascoin and Slavi C. Sevov

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556-5670, USA

Received 28 February 2003; received in revised form 5 May 2003; accepted 17 May 2003

Abstract

The title compound was prepared by direct fusion of the corresponding elements at 800°C followed by slow cooling to room temperature. It crystallizes in the orthorhombic space group Pbcm (No. 57) with a = 11.340(2), b = 8.745(2), and c = 14.920(2) Å, V = 1479.8(5) Å³, and Z = 4. The structure is made of isolated V-shaped trimers As³⁻ and sodium and barium countercations. According to magnetic and resistivity measurements, Na₄Ba₃As₆ is a narrow-gap semiconductor, i.e. a closed-shell compound that fulfills the Zintl concept.

Keywords: Zintl phases; Arsenides; Isolated oligomorphic anions of arsenic

1. Introduction

Over the past decade, numerous compounds have been discovered in the binary systems of an alkali metal and a p-block element [1]. Often, their compositions are as simple as their structural features are striking and unpredictable. The heavier elements of groups 13 (Ga, In, Tl) and 14 (Si, Ge, Sn, Pb) have shown unexpected capability to form "naked" clusters with delocalized bonding such as In₇⁺, Ti₇⁺, Ge₅⁺, Sn₅⁺, etc. [1,2]. The use of two or more different alkali or alkaline-earth metals as countercations provides yet another synthetic approach to further expand the already large number of such clusters. Different cations bring different packing requirements as well as reducing capability because of their different sizes, charges and electronegativity. Thus, the novel clusters Ti⁵⁺, Ti⁶⁺, Ti₁⁰⁺, Ti₁₂⁺, Sn₁⁰⁺, Sn₁₂⁺, Sn₈⁻, etc., are known only with such mixed cations (1d). Similar negatively charged clusters with delocalized bonding are not known for the electron-rich pnictogens (Pn=P, As, Sb, Bi), they are usually found as isolated atoms, Pn³⁻, or as various oligomers, infinite chains, and layers bonded by regular 2-center–2-electron bonds [3]. We recently reported the synthesis and characterization of pnictogen oligomers with conjugated π-electron systems, flat zigzag tetramers Pn⁴⁺⁻ and dimers Bi²⁺⁺ in the metallic A₃Pn₄ and A₃Bi₂ (A=K, Rb, Cs), respectively [4]. Using alkali and alkaline-earth cations we attempted the synthesis of a similar trimer Pn³⁻. Such a phosphorus trimer was reported in the compound K₄P₃ but was considered to be a radical, P₃⁻⁻ [5]. Our aim was to investigate whether a similar trimer of arsenic in an analogous compound A₄As₃ would behave as a radical or the extra electron could be delocalized making the compound metallic just as A₃Pn₄ and A₃Pn₂. These attempts led to the synthesis of the title compound with a new σ-bonded trimer As₃⁻⁻.

2. Experimental section

2.1. Synthesis

All manipulations were performed in an Argon-filled glove box with typical moisture level below 1 ppm or under vacuum. The starting materials Na (Alfa Aesar, 99.9% metal basis), and arsenic (Strem, 99.99%) were used as received, while Ba (Acros, 99+%) was first cleaned of its protective oil by multiple rinsing in hexane under nitrogen. In a typical reaction an appropriate mixture of the elements is loaded in a tubular niobium container that is subsequently sealed by arc welding.
under argon. The container is then enclosed in a fused-silica ampoule which, in turn, is evacuated and flame sealed. The assembly is heated at various temperature regimes. The title compound was initially isolated from a reaction with a nominal composition Na₄Ba₃As₆ designed to produce \( \text{As}^{3-} \). The title compound was isolated from a mixture of sodium–barium–arsenic mixtures by heating at various temperatures under argon. The container is then enclosed in a fused-silica ampoule which, in turn, is evacuated and flame sealed. The assembly is heated at various temperature regimes. The title compound was initially isolated from a reaction with a nominal composition Na₄Ba₃As₆ designed to produce \( \text{As}^{3-} \). Later, Na₄Ba₃As₆ was made as a pure phase from a reaction mixture of the same composition and using the same temperature sequence. The compound crystallizes as dark-gray to black, shiny, and brittle small plates. It should be mentioned that the sodium–barium–arsenic mixtures do not seem to attack the niobium containers, while mixtures of the heavier alkali metals usually react with niobium and form negatively charged niobium–arsenic species [6].

2.2. Structure determination

Crystals of the compound were selected inside a dry-box equipped with a microscope. They were then sealed in thin-walled glass capillaries and were checked for singularity and quality on an Enraf-Nonius CAD4 single crystal diffractometer (MoKα, \( \lambda = 0.71073 \text{ Å} \)). An octant of data was collected (\( \omega = 20°, 2\theta_{\max} = 50° \)) of the best one (0.12 × 0.12 × 0.04 mm³) at room temperature. The structure was solved by direct methods and refined (on \( F^2 \)) in the orthorhombic space group \( Pbcm \) with the aid of the SHELXTL V5.1 software package [7]. Details of the data collection and refinement are given in Table 1.

2.3. Magnetic measurements

Twenty-eight milligrams of Na₄Ba₃As₆ were sealed in a fused-silica tube between two tightly fitting rods of the same material. The magnetization of this sample was measured on a MPMS SQUID magnetometer at a filed of 3 T over a temperature range of 10–250 K. After correction for the holder and for ion core diamagnetism the molar susceptibility was negative and temperature independent over the whole range, \( -3.2(1) \times 10^{-4} \text{ emu/mol} \). This is consistent with a diamagnetic compound.

2.4. Electrical resistivity measurements

The electrical resistivity of the compound was measured by the four-probe method (an in-line probe from Jandel) on a pressed pellet (4000 psi, 1 mm thick, 13 mm diameter) over the temperature range 205–275 K inside the cold well of a dry box. A constant current of 153.29 mA was applied to the sample and the drop of the voltage was measured. The resistivity decreases at increasing temperature, a behavior consistent with a semiconducting compound.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Selected data collection and refinement parameters for Na₄Ba₃As₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>Na₄Ba₃As₆</td>
</tr>
<tr>
<td>fw</td>
<td>953.50</td>
</tr>
<tr>
<td>Space group, Z</td>
<td>( Pbcm ), 4</td>
</tr>
<tr>
<td>Unit cell parameters</td>
<td>( a = 11.340(2) \text{ Å} ), ( b = 8.736(3) \text{ Å} ), ( c = 14.920(2) \text{ Å} ), ( V = 1479.8(5) \text{ Å}^3 )</td>
</tr>
<tr>
<td>Radiation</td>
<td>MoKα, 0.71073 Å</td>
</tr>
<tr>
<td>Temp</td>
<td>293 K</td>
</tr>
<tr>
<td>Abs coeff</td>
<td>212.82 cm⁻¹</td>
</tr>
<tr>
<td>Density (calcd)</td>
<td>4.280 g/cm³</td>
</tr>
<tr>
<td>Total reflections/parameters</td>
<td>1362/67</td>
</tr>
<tr>
<td>R indices (I &gt; 2σ(I))</td>
<td>1057</td>
</tr>
<tr>
<td>Residual peaks</td>
<td>1.940/–1.259</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>1.899, wR2 = 8.80%</td>
</tr>
<tr>
<td>wR2 for ( F^2 &gt; 2\sigma(F^2) ), w = ( [\Sigma w(Fo^2) - \Sigma w(Fc^2)]^2 )/ ( \Sigma w(Fo^2) )</td>
<td>9.54%</td>
</tr>
</tbody>
</table>
| 3. Results and discussion

The structure of the title compound is made of isolated bent arsenic trimers, \( \text{As}^{3-} \), that are separated by sodium and barium cations (Fig. 1). There are two crystallographically different but otherwise very similar trimers in the structure, As₁–As₂–As₁ (type 1) and As₃–As₄–As₃ (type 2). The shortest inter-trimer distances occur between trimers of the same type and define the neighboring trimers of the same type and define the non-existence of similar antimony compound. Thus, reactions designed to produce Na₄Ba₃Sb₆ yielded a mixture of Na₃Ba₃Sb₄ with isolated dimers of Sb ± [8] and NaSb with infinite helical chains of Sb⁻ [9].

The As–As distances within the trimers, 2.470(1) and 2.480(1) Å in types 1 and 2, respectively, are in very good agreement with single-bond distances observed in other
compounds, 2.511(3) and 2.563(3)Å for As$_2^4$ in Na$_2$Sr$_3$As$_4$ [10], 2.474(2)–2.579(2)Å for the helical tetramers of As$_4^6$ in Ca$_2$As$_3$ [11], and 2.465(1)–2.497(2)Å for the infinite chains in $A$As ($A = \text{Na, K, Rb}$) [12]. The angles of the trimers, 114.16(7)$^\circ$ for type 1 and 115.33(7)$^\circ$ for type 2, are somewhat larger than expected when compared to those observed in Ca$_2$As$_3$, 105.1, 108.6, 110.2 and 111.5$^\circ$. However, such large angles are not unusual, 116.3$^\circ$ is found for the helical tetramer of As$_4^6$ in Sr$_3$As$_4$ [13], and are perhaps greatly influenced by the type of the cations and the packing efficiency.

The electronic structure of Na$_4$Ba$_3$As$_6$ follows smoothly the Zintl concept. Formal charges of 1- and 2- for the terminal one-bonded and the central two-bonded arsenic atoms, respectively, are easily assigned. Applying this simple bonding scheme, the trimers can be then formulated as [(1b–As$_2^4$/C0)(2b–As$^2$/C0)(1b–As$_2^4$/C0)].

Often compounds are classified as Zintl phases based only on their structures, i.e. without further investigation of their physical properties. Nevertheless, since many such phases have been later found to be metallic, electrical resistivity and magnetization should be measured when possible. The magnetic measurements of Na$_4$Ba$_3$As$_6$ showed negative and temperature independent molar magnetic susceptibility, $-3.2(1) \times 10^{-4}$emu/mol over the range 10–250 K (Fig. 3a). However, since the absolute values of the magnetic susceptibility of both diamagnetic (semiconducting) and Pauli-paramagnetic (metallic) compounds are usually very small, defining the character of the compound is often quite ambiguous. An additional test such as electrical conductivity is very helpful in such situations, but such measurements for air-sensitive compounds are often difficult to manage. Thus, the resistivity of Na$_4$Ba$_3$As$_6$ was measured by the four-probe method inside the cold well of a dry box. The resistivity was measured to be ca. 1376(14)Ω cm at room temperature and increased with decreasing temperature (Fig. 3b), an indication for a semiconducting behavior. Furthermore, the plot of ln(ρ) versus the reciprocal temperature was found to be linear in the range 205–274 K (Fig. 3b) and the corresponding energy gap was calculated to be 0.180(2)eV. Consequently, based
on these two measurements Na$_4$Ba$_3$As$_6$ is indeed a close shell compound and a narrow band gap semiconductor, a “true” Zintl phase.

Acknowledgments

We thank the National Science Foundation (CHE-0098004) for the financial support.

References