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# Synthesis and characterization of the Zintl phase $\text{Na}_4\text{Ba}_3\text{As}_6$ with isolated $\text{As}_3^{5-}$ anions

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## 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,  $V = 1479.8(5)$  Å<sup>3</sup>, and  $Z = 4$ . The structure is made of isolated V-shaped trimers  $\text{As}_3^{5-}$  and sodium and barium counteranions. According to magnetic and resistivity measurements,  $\text{Na}_4\text{Ba}_3\text{As}_6$  is a narrow-gap semiconductor, i.e. a closed-shell compound that fulfills the Zintl concept.

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## 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  $\text{In}_{11}^{7-}$ ,  $\text{Tl}_6^{6-}$ ,  $\text{Tl}_7^{7-}$ ,  $\text{Ge}_9^{4-}$ ,  $\text{Sn}_9^{4-}$ , etc. [1,2]. The use of two or more different alkali or alkaline-earth metals as counteranions 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  $\text{Tl}_5^{7-}$ ,  $\text{Tl}_9^{9-}$ ,  $\text{Tl}_{13}^{10-}$ ,  $\text{Tl}_6^{8-}$ ,  $\text{Sn}_{12}^{12-}$ ,  $\text{Sn}_8^{6-}$ , etc., are known only with such mixed cations (1d). Similar negatively charged clusters with delocalized bonding are not known for the electron-rich pnictogens ( $Pn = \text{P, As, Sb, Bi}$ ), they are usually found as isolated atoms,  $Pn^{3-}$ , 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

$\pi$ -electron systems, flat zigzag tetramers  $Pn_4^{(4+\delta)-}$  and dimers  $\text{Bi}_2^{(2+\delta)-}$  in the metallic  $A_5Pn_4$  and  $A_3\text{Bi}_2$  ( $A = \text{K, Rb, Cs}$ ), respectively [4]. Using alkali and alkaline-earth cations we attempted the synthesis of a similar trimer  $Pn_3^{3-}$ . Such a phosphorus trimer was reported in the compound  $\text{K}_4\text{P}_3$  but was considered to be a radical,  $\text{P}_3^{4-}$  [5]. Our aim was to investigate whether a similar trimer of arsenic in an analogous compound  $A_4\text{As}_3$  would behave as a radical or the extra electron could be delocalized making the compound metallic just as  $A_5Pn_4$  and  $A_3Pn_2$ . These attempts led to the synthesis of the title compound with a new  $\sigma$ -bonded trimer  $\text{As}_3^{5-}$ .

## 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

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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  $\text{Na}_2\text{BaAs}_3$  designed to produce “ $\text{As}_3^{4-}$ ” (heated for 12 h at  $800^\circ\text{C}$  and then cooled at a rate of  $5^\circ\text{C/h}$ ) analogous to “ $\text{P}_3^{4-}$ ”. Later,  $\text{Na}_4\text{Ba}_3\text{As}_6$  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 ( $\text{MoK}\alpha$ ,  $\lambda = 0.71073 \text{ \AA}$ ). An octant of data was collected ( $\omega - 2\theta$ ,  $2\theta_{\text{max}} = 50^\circ$ ) of the best one ( $0.12 \times 0.12 \times 0.04 \text{ mm}^3$ ) 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 milligram of  $\text{Na}_4\text{Ba}_3\text{As}_6$  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 field 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 1  
Selected data collection and refinement parameters for  $\text{Na}_4\text{Ba}_3\text{As}_6$

Empirical formula	$\text{Na}_4\text{Ba}_3\text{As}_6$
fw	953.50
Space group, $Z$	$Pbcm$ , 4
Unit cell parameters	$a = 11.340(2) \text{ \AA}$ $b = 8.736(3) \text{ \AA}$ $c = 14.920(2) \text{ \AA}$ $V = 1479.8(5) \text{ \AA}^3$
Radiation	$\text{MoK}\alpha$ , $0.71073 \text{ \AA}$
Temp	293 K
Abs coeff	$212.82 \text{ cm}^{-1}$
Density (calcd)	$4.280 \text{ g/cm}^3$
Total reflections/parameters	1362/67
Obs independent reflections ( $I > 2\sigma_I$ )	1057
$R$ indices ( $I > 2\sigma_I$ ) <sup>a</sup>	$R_1 = 3.89\%$ , $wR_2 = 8.80\%$
$R$ indices (all data)	$R_1 = 5.86\%$ , $wR_2 = 9.54\%$
Residual peaks	$1.940/-1.259 e/\text{\AA}^3$

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|},$$

$$wR_2 = \left\{ \frac{[\sum w[(F_o)^2 - (F_c)^2]^2]}{[\sum w(F_o^2)]} \right\}^{1/2} \text{ for } F_o^2 > 2\sigma(F_o^2), w = \frac{1}{[\sigma^2(F_o)^2 + (0.0487P)^2 + 0.8553P]} \text{ where } P = [(F_o)^2 + 2(F_c)^2]/3.$$

## 3. Results and discussion

The structure of the title compound is made of isolated bent arsenic trimers,  $\text{As}_3^{5-}$ , 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 types,  $3.827(2)$  and  $4.354(2) \text{ \AA}$  between types 1 and types 2 trimers (related by a  $2_1$  along  $c$ ), respectively. Both values are greater than twice the van der Waals radius of arsenic,  $3.70 \text{ \AA}$ , hence no direct trimer–trimer interactions are expected. The sodium and barium cations are arranged highly symmetrically around the trimers and envelope them completely (Fig. 2). Each As–As bond is “bridged” by four cations and the middle arsenic atom is additionally coordinated by one more cation. The end arsenic atoms are also coordinated by additional cations, four at As1 and three at As3 (Fig. 2). Furthermore, the four cations at As1 are all sodium while two sodium and a barium are found at As3. These cations coordinate also to the neighboring trimers of the same type and define the inter-trimer distances, smaller between type 1 due to the smaller sodium cations and larger between type 2 due to the larger barium. These specific arrangements of the cations may explain the non-existence of similar antimony compound. Thus, reactions designed to produce  $\text{Na}_4\text{Ba}_3\text{Sb}_6$  yielded a mixture of  $\text{Na}_2\text{Ba}_3\text{Sb}_4$  with isolated dimers of  $\text{Sb}_2^{4-}$  [8] and NaSb with infinite helical chains of  $\text{Sb}^-$  [9].

The As–As distances within the trimers,  $2.470(1)$  and  $2.480(1) \text{ \AA}$  in types 1 and 2, respectively, are in very good agreement with single-bond distances observed in other

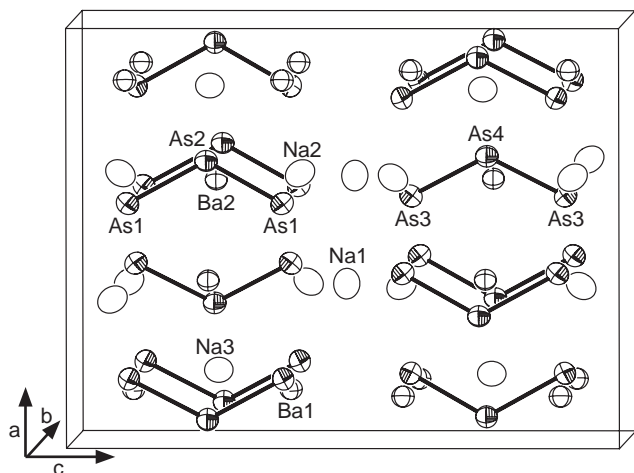


Fig. 1. ORTEP drawing of the structure of  $\text{Na}_4\text{Ba}_3\text{As}_6$  (thermal ellipsoids at the 90% probability level, the unit cell is outlined). The arsenic trimers ( $C_{2v}$ ) are well separated by sodium and barium cations. Distances (Å) and angles (deg): As1–As2 2.470(1), As3–As4 2.480(1), As1–As2–As1 114.16(7), As3–As4–As3 115.33(7).

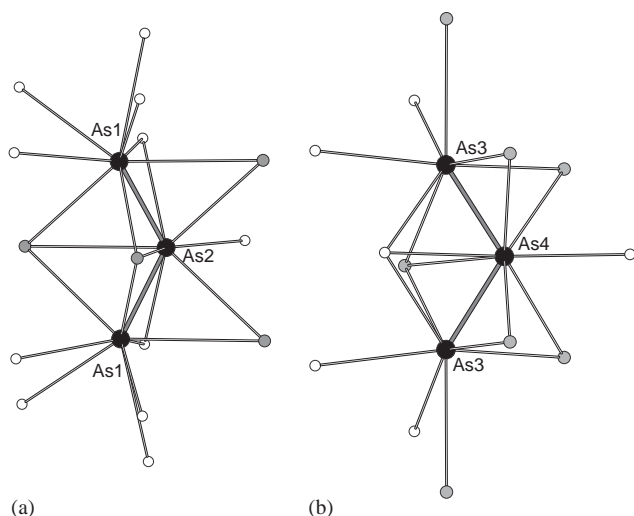


Fig. 2. Shown is the arrangements of cations (Ba in gray and Na in white circles) around the trimers of: (a) type 1 and (b) type 2. Each As–As bond is bridged by four cations (3 Ba and 1 Na) and an additional sodium cation is coordinated to the middle arsenic for both dimer types. Four more sodium cations are coordinated to As1 while two additional sodium and a barium cation are found around As3.

compounds, 2.511(3) and 2.563(3) Å for  $\text{As}_2^{4-}$  in  $\text{Na}_2\text{Sr}_3\text{As}_4$  [10], 2.474(2)–2.579(2) Å for the helical tetramers of  $\text{As}_4^{6-}$  and helical octamers of  $\text{As}_8^{10-}$  in  $\text{Ca}_2\text{As}_3$  [11], and 2.465(1)–2.497(2) Å for the infinite chains in  $A\text{As}$  ( $A = \text{Na}, \text{K}, \text{Rb}$ ) [12]. The angles of the trimers, 114.16(7)° for type 1 and 115.33(7)° for type 2, are somewhat larger than expected when compared to those observed in  $\text{Ca}_2\text{As}_3$ , 105.1, 108.6, 110.2 and 111.5°. However, such large angles are not unusual, 116.3° is found for the helical tetramer of  $\text{As}_4^{6-}$  in  $\text{Sr}_3\text{As}_4$  [13], and are perhaps greatly influenced by the type of the cations and the packing efficiency.

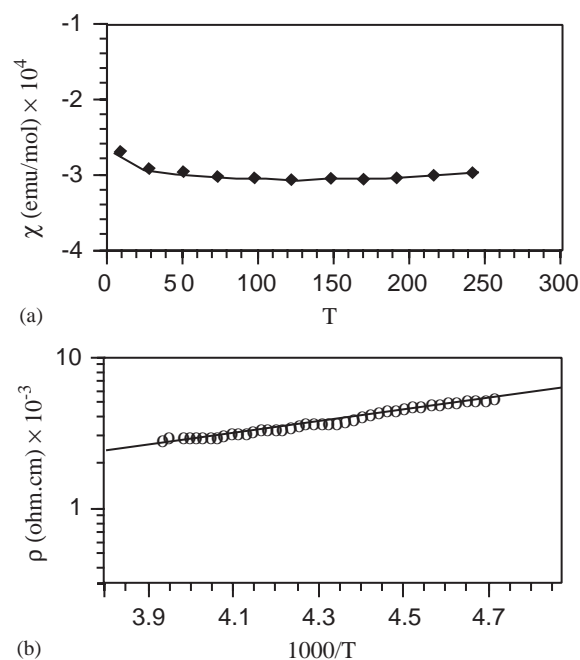


Fig. 3. Plots of: (a) the magnetic susceptibility and (b) the electrical resistivity versus temperature for  $\text{Na}_4\text{Ba}_3\text{As}_6$ .

The electronic structure of  $\text{Na}_4\text{Ba}_3\text{As}_6$  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  $[(1b\text{-As}^{2-})(2b\text{-As}^{-})(1b\text{-As}^{2-})]$ .

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  $\text{Na}_4\text{Ba}_3\text{As}_6$  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  $\text{Na}_4\text{Ba}_3\text{As}_6$  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  $\ln(\rho)$  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  $\text{Na}_4\text{Ba}_3\text{As}_6$  is indeed a close shell compound and a narrow band gap semiconductor, a “true” Zintl phase.

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### References

- [1] (a) H. Schäfer, B. Eisenmann, W. Müller, *Angew. Chem. Int. Ed.* 12 (1973) 694.  
 (b) H. Schäfer, *Annu. Rev. Mater. Sci.* 15 (1985) 1.  
 (c) J.D. Corbett, *Chem. Rev.* 85 (1985) 383.  
 (d) J.D. Corbett, *Angew. Chem. Int. Ed.* 39 (2000) 670.  
 (e) J.D. Corbett, *Inorg. Chem.* 39 (2000) 5178.
- [2] S. Kauzlarich (Ed.), *Structure and Bonding of Zintl Phases and Ions*, VCH Publishers Inc., New York, 1996.
- [3] (a) G.A. Papoian, R. Hoffmann, *Angew. Chem. Int. Ed.* 39 (2000) 2048.  
 (b) H. Schäfer, B. Eisenmann, *Rev. Inorg. Chem.* 3 (1981) 29.  
 (c) B. Eisenmann, G. Cordier, in: S. Kauzlarich (Ed.), *Chemistry and Bonding of Zintl Ions*, VCH Publishers Inc, New York, 1996, p. 61.
- [4] F. Gascoin, S.C. Sevov, *J. Am. Chem. Soc.* 122 (2000) 10251;  
 F. Gascoin, S.C. Sevov, *Inorg. Chem.* 40 (2001) 5177.
- [5] H.G. von Schnering, M. Hartweg, U. Hartweg, W. Höhle, *Angew. Chem. Int. Ed.* 28 (1989) 56.
- [6] (a) F. Gascoin, S.C. Sevov, *Inorg. Chem.* 41 (2002) 5920.  
 (b) F. Gascoin, S.C. Sevov, *Inorg. Chem.* 41 (2002) 2820.  
 (c) F. Gascoin, S.C. Sevov, *Angew. Chem. Int. Ed.* 41 (2002) 1232.  
 (d) J. Nuss, R.H. Cardoso Gil, W. Höhle, K. Peters, H.G. von Schnering, *Z. Anorg. Allg. Chem.* 622 (1996) 1854.  
 (e) F. Gascoin, S.C. Sevov, *Inorg. Chem.* 42 (2003) 904.
- [7] (a) Bruker Analytical X-ray Systems, Inc., Madison, WI, 1997.  
 (b) N. Walker, D. Stuart, *Acta Crystallogr.* A39 (1983) 158.
- [8] L. Chi, J.D. Corbett, *J. Solid State Chem.* 162 (2001) 327.
- [9] D.T. Cromer, *Acta Crystallogr.* 12 (1959) 41.
- [10] K. Vidyasagar, W. Höhle, H.G. von Schnering, *J. Alloys Compd.* 235 (1996) 37.
- [11] K. Deller, B. Eisenmann, *Z. Naturforsch.* 31b (1976) 1023.
- [12] W. Höhle, H.G. von Schnering, *Acta Crystallogr.* 34A (1978) S152.
- [13] K. Deller, B. Eisenmann, *Z. Naturforsch.* 32b (1977) 1368.