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Stefanie Dehnen, Susanne Burtzlaff, Malgorzata Holynska. Synthesis and crystal structures of K_2SnAs_2 and a new modification of NaAs. *Journal of Inorganic and General Chemistry / Zeitschrift für anorganische und allgemeine Chemie*, 2010, 636 (9-10), pp.1691. <10.1002/zaac.201000050>. <hal-00599855>

HAL Id: hal-00599855

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Submitted on 11 Jun 2011

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Synthesis and crystal structures of K_2SnAs_2 and a new modification of NaAs

Journal:	<i>Zeitschrift für Anorganische und Allgemeine Chemie</i>
Manuscript ID:	zaac.201000050.R1
Wiley - Manuscript type:	Communication
Date Submitted by the Author:	12-Feb-2010
Complete List of Authors:	Dehnen, Stefanie; Philipps-Universität Marburg, Fachbereich Chemie Burtzloff, Susanne; Philipps-Universität Marburg, Fachbereich Chemie Holynska, Malgorzata; Philipps-Universität Marburg, Fachbereich Chemie
Keywords:	Zintl phases, Crystal structure, Binary Anions, Pnictogenido Stannates



SHORT COMMUNICATION

DOI: 10.1002/zaac.200((will be filled in by the editorial staff))

Synthesis and crystal structures of K_2SnAs_2 and a new modification of NaAsSusanne Burtzloff,^[a] Małgorzata Hołyńska,^[a] and Stefanie Dehnen*^[a]*Dedicated to Professor Bernd Harbrecht on the occasion of his 60th birthday.***Keywords:** Zintl phases / Crystal structure / Binary Anions / Pnictogenido Stannates

Solid state reactions of K or Na with Sn and As have resulted in the formation of a new ternary Zintl phase, K_2SnAs_2 (**1**) and a new modification of the binary Zintl phase NaAs (**2**), the syntheses and structures we report herein. **1** is described in the orthorhombic space group *Cccm* with the unit cell dimensions $a = 14.653(5)$, $b = 25.415(6)$, $c = 6.953(4)$ Å, $V = 2589(2)$ Å³ at 203 K, $R(int) = 0.1686$ and final R values $R1 = 0.0780$ ($I > 2\sigma(I)$); $wR2 = 0.1810$

(all data)). **2** crystallizes in the monoclinic space group $P2_1/c$ and accords to the LiAs structure type with the unit cell dimensions $a = 6.242(9)$, $b = 5.849(7)$, $c = 11.55(2)$, Å, $\beta = 117.1(2)^\circ$, $V = 375(1)$ Å³ at 173 K, $R(int) = 0.0812$ and final R values $R1 = 0.0677$ ($I > 2\sigma(I)$); $wR2 = 0.1541$ (all data).

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Introduction

Although having been systematically investigated for nearly 80 years, Zintl phases still represent a hot topic in recent inorganic research. In the meantime, the pioneer work by Zintl himself¹ was enriched by first structural investigations in the 1970ies² and further extended by the synthesis and characterization of phases containing binary anions of different combinations of main group (semi-)metals.³ Very recently, another dimension of Zintl anions was added by the investigation of intermetalloid Zintl anions – both binary and ternary variations.⁴

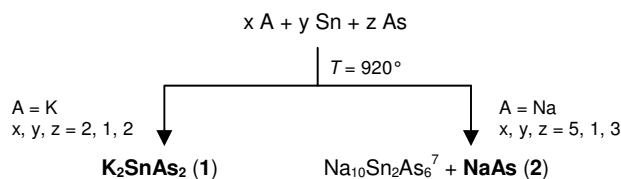
Depending on the combination of main group element atoms in binary Zintl anions, the resulting phases show very different chemical and physical properties. Having intensely studied the syntheses, structures and reactivity of binary Group 14/16 anions,⁵ one of our current aims is the investigation of Group 14/15 anions with regard to their synthesis and structures and with regards to their reactivity toward transition metal complexes. We have recently shown that the latter provides an approach toward ternary intermetalloid Zintl anions.⁶

Herein we report synthesis and structures of one new compound and one new modification of a known one, that yielded from reactions of alkali metals with Sn and As at high temperatures, the ternary Zintl phase K_2SnAs_2 (**1**) and a new example of the binary Zintl phase NaAs (**2**), which was observed in low yield beside the known ternary phase $Na_{10}Sn_2As_6$.^{7a} These investigations serve to add new results to comprehensive work by further working groups.⁷

Results and Discussion

Compounds **1** and **2** were obtained under similar reaction conditions with the difference of the alkali metal used. Surprisingly,

the crystalline product of the reaction with Na did not only comprise a ternary salt but also a binary Zintl phase. Scheme 1 summarizes the synthesis of **1** and **2**.



Scheme 1. Schematic synthesis pathways for compounds **1** and **2** at high temperatures. For details of the reaction conditions see the *Experimental Section*.

Compound **1** was refined in the orthorhombic space group *Cccm* (no. 66) with $a = 14.653(5)$, $b = 25.415(6)$, $c = 6.953(4)$ Å, $V = 2589(2)$ Å³ and $Z = 8$.⁸ Compound **2** crystallizes in the monoclinic space group $P2_1/c$ (no. 14) with $a = 6.242(9)$, $b = 5.849(7)$, $c = 11.55(2)$, Å, $\beta = 117.1(2)^\circ$, $V = 375(1)$ Å³ and $Z = 4$. The crystal structures of **1** and **2** are depicted in figures 1 and 2, respectively.

In **1**, the Sn and As atoms form one-dimensional chains along the crystallographic *c* axis by *trans*-edge sharing $[SnAs_4]$ tetrahedra. This motif is known from several binary atomic arrangements, among them the neutral prototype SiS_2 structure,⁹ the $[InTe_2]^-$ anion in $AlnTe_2$ ($A = Na, K, Rb, Tl$)¹⁰ or the $[FeS_2]^-$ anion in $KFeS_2$,¹¹ all of which are isoelectronic to the $[SnAs_2]^{2-}$ substructure in **1**. For binary Group 14/15 anions, several analogues of **1** have been reported, among them the isostructural heavier homologue, Cs_2SnAs_2 ^{12a} and the lighter homologue Rb_2SiAs_2 (space group *Ibam*).^{12b} We checked if it would be possible to refine **1** assuming the smaller cell as for Cs_2SnAs_2 ^{12a} and the reported atomic coordinates. Both the attempt to solve the structure and to refinement the structure in *Ibam* were not successful, which suggests that **1** is not isomorphous with several reported salts besides Cs_2SnAs_2 , such as Cs_2MnSe_2 ,^{12c} K_2MnTe_2 ,^{12c} Rb_2MnTe_2 ,^{12c} Cs_2SiAs_2 ^{12a} and K_2ZnTe_2 .^{12d} In the orthorhombic space group *Cccm* there are three symmetry-independent $\{[SnAs_2]^{2-}\}_n$ chains, in one of which (Sn1, As1a-1d) the As atoms

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are disordered (four disordered components with site occupancies of 0.125 each). The parameters of the ordered $[\text{SnAs}_2]$ chains (Sn2, As2 and Sn3, As3, As4; Sn–As 2.620(3)–2.628(4) ppm, Sn...Sn 347.6(2)–349.8(9) ppm; As–Sn–As 96.9(1)–97.5(2) $^\circ$) are very similar to those reported for Cs_2SnAs_2 (Sn–As 263.1(1) pm, Sn...Sn 347.7(2) pm; As–Sn–As 97.28(1) $^\circ$).^{12a} The anionic chains are stabilized and held together by interactions with the K^+ ions in between.

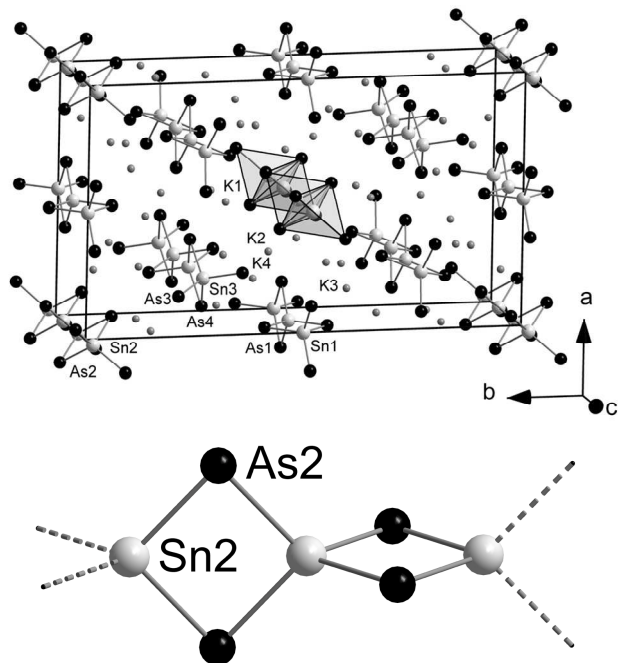


Figure 1. General features of the crystal structure of **1**. Fragment of the crystal structure (top, omitting disorder for clarity) and of one of the three crystallographically independent $\{[\text{SnAs}_2]^{2-}\}_n$ chains running along the crystallographic c axis (bottom). Selected distances /pm and angles $^\circ$: Sn–As 2.620(3)–2.628(4) ppm, Sn...Sn 347.6(2)–349.8(9) ppm, As–Sn–As 96.9(1)–97.5(2) $^\circ$

The new modification of NaAs adopts the LiAs structure type.¹³ As shown in figure 2, **2** contains infinite, idealized 4_1 chains of two-coordinate, formal As^- atoms, as observed for the known modification of NaAs,¹⁴ that crystallizes in the NaP structure type,¹⁵ thus in the space group $P2_12_12_1$. In this type, the idealized 4_1 helices, that possess crystallographic 2_1 symmetry, all show the same rotational sense within the crystal. In contrast, the $\{[\text{As}]^-\}_n$ chains in **2**, that equally show crystallographic 2_1 symmetry, are alternately right handed (around $[0,b,0]$) or left handed (around $[\frac{1}{2},b,\frac{1}{2}]$). The As–As distances in **2** (245.5(5) – 248.4(4) pm) correspond well to the reported ones (246.5 pm on average). Whereas the As–As–As angles (109.2(2) and 111.6(2) $^\circ$) in **2** are slightly smaller than those in the known NaAs structure (111.9 $^\circ$ and 114.8 $^\circ$), the As–As–As–As torsion angles are identical in both modifications (**2**: 54.5(2) – 68.3(2) $^\circ$; reported: 54.2 – 68.3 $^\circ$). The latter clearly demonstrates the derivation of the helical structures from a 4_1 symmetry in both structures.

The Na ions in **2** are located between the As helices. In the NaP-type NaAs, they form one-dimensional helices that run through the crystal along $[1,0,0]$, perpendicular to the $\{[\text{As}]^-\}_n$ chains along $[0,1,0]$. Different to that, they form planar four-ring arrangements (Na1 – Na2(x, 1.5–y, 0.5+z) – Na1(1–x, 1–y, 1–z) – Na2(1–x, y–0.5, 0.5–z); Na...Na 331(2) – 345(2) pm) that are topologically connected via *trans*-corners (Na2...Na2(–x, 1–y, –z) 330(2) pm), and run through the crystal in a declined manner between the $\{[\text{As}]^-\}_n$

helices. The Na...As interactions lead to c.n. = 8 for the As atoms (AsAs₂...Na₆; As...Na 299(1) – 314(1) pm). *Vice versa*, Na atoms possess c.n. = 6.

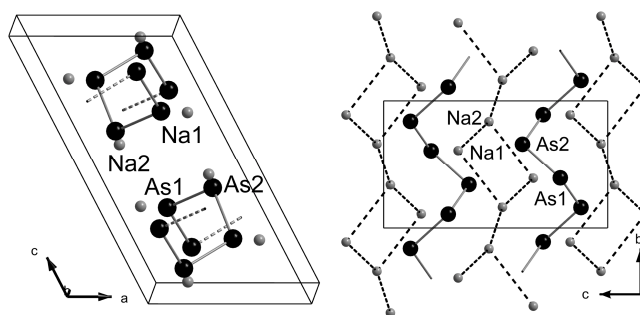


Figure 2. Figure 2. Fragment of the crystal structure of **2** approximately along crystallographic b axis (left hand side) and arrangement of the Na^+ ions (right hand side). Selected distances /pm and angles $^\circ$: As–As 245.5(5) – 248.4(4), As...As (along b) 584.9(7), As...Na 299(1) – 314(1), Na...Na 331(2) – 345(2); As–As–As 109.2(2) – 111.6(2).

For the synthesis of **1**, we did not detect binary by-products – at least no crystalline ones. However, in this case the product corresponded to the stoichiometry of the reactants. The stoichiometry used for the synthesis of **2** also accorded exactly to the atomic ratio within the desired – known – product $\text{K}_{10}\text{Sn}_2\text{As}_6$. Therefore, reactions of Na with the SiO_2 walls of the quartz tube have probably led to a change in the available amount of elements and enabled the generation of the by-product **2** in low yields.

Conclusions

The attempt to synthesize ternary Zintl phases containing binary $[\text{Sn}_x\text{As}_y]^{4-}$ anions led to the formation of the new compound K_2SnAs_2 and a new modification of the binary Zintl phase NaAs in low yields beside a known ternary salt. Both structures comprise chains of 1-dimensionally extended Zintl anions; different to the known NaAs modification, the one reported herein adopts the LiAs structure type with the idealized 4_1 helices of the $\{[\text{As}]^-\}_n$ strands according to two different rotational senses.

Experimental Section

Synthesis of 1: Potassium metal (1.978 g, 46.1 mmol) and tin (2.744 g, 23.1 mmol) were combined in a Quartz ampoule under argon and melted by heating up using a Bunsen burner. Upon cooling down to room temperature, 2 molar equivalents of arsenic – with respect to Sn – (3.458 g, 46.1 mmol) were added and the mixture was heated to melt again. In order to gain a homogenous phase, 0.500 g (1.4 mmol) of the crude product was pulverized within a glove-box, transferred into a second Quartz ampoule that was subsequently sealed under high vacuum, and tempered in a high-temperature oven (50 $^\circ\text{C}\cdot\text{h}^{-1}$ to 920 $^\circ\text{C}$, 2 h at 920 $^\circ\text{C}$, 30 $^\circ\text{C}\cdot\text{h}^{-1}$ to room temperature. Dark needles with metallic glance of **1** were obtained in near quantitative yield (99%).

Synthesis of 2: Sodium metal (2.206 g, 95.9 mmol) and tin (2.070 g, 17.4 mmol) were combined in a Quartz ampoule under argon and melted by heating up using a Bunsen burner. Upon cooling down to room temperature, 3 molar equivalents of arsenic – with respect to Sn – (3.920 g, 52.3 mmol) were added and the mixture was heated to melt again. A dark product with metallic glance results. Beside known $\text{Na}_{10}\text{Sn}_2\text{As}_6^{\text{LIT}}$ as the main product, crystals of **2** were obtained in low yield (8%).

X-ray Crystallography: Data collection was performed on a STOE IPDS-I (1) or STOE-IPDS-II (2) diffractometer with graphite-monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) at 203 K (1) or 173 K (2). (1) was solved by Patterson method and refined on F^2 by full-matrix least-squares methods using the SHELXTL program package.¹⁶ In case of (2) the atomic coordinates were taken directly from literature¹³ for the sake of simplified comparison. Crystal data for K₂SnAs₂ (1, M = 346.73 g·mol⁻¹): 1 is described in the orthorhombic space group *Cccm* (no. 66), $a = 14.653(5)$, $b = 25.415(6)$, $c = 6.953(4) \text{ \AA}$, $V = 2589(2) \text{ \AA}^3$ at 203 K, $Z = 8$, $D_c = 3.558 \text{ g·cm}^{-3}$, $\mu = 15.23 \text{ mm}^{-1}$, 6147 reflections measured ($R(\text{int}) = 0.1686$), 850 unique, 578 with $I > 2\sigma(I)$ and final R values $R1 = 0.0780$ ($I > 2\sigma(I)$); $wR2 = 0.1810$ (all data)). The data are affected by twinning and/or intergrowth of the needle-type crystals; therefore several models have been tested: 1 was solved in the triclinic space group *P*-1 ($a = 6.953$, $b = 14.631$, $c = 14.653 \text{ \AA}$; $\alpha = 60.28$, $\beta = 89.96$, $\gamma = 89.86^\circ$). Subsequently the structure was transformed to the monoclinic space group *C2/c* ($a = 14.653$, $b = 25.413$, $c = 6.953 \text{ \AA}$; $\beta = 90.04^\circ$; transformation matrix by rows: 0 0 -1, 0 2 -1, 1 0 0). Next the space group was switched to the *Cccm* reported in the text (transformation matrix by rows: -1 0 0, 0 1 0, 0 0 -1). At this stage another transformation is possible to *P6/mcc* (origin shift to 0.5 0 0, transformation matrix by rows: -1 1 0, 0 2 0, 0 0 -1). In all solutions the structure general features (described in text) persist. Crystal data for NaAs (2, M = 97.91 g·mol⁻¹): monoclinic, space group *P2₁/c* (no. 14), $a = 6.242(9)$, $b = 5.849(7)$, $c = 11.55(2) \text{ \AA}$, $\beta = 117.1(2)^\circ$, $V = 375(1) \text{ \AA}^3$, $Z = 4$, $D_c = 3.465 \text{ g·cm}^{-3}$, $\mu = 17.76 \text{ mm}^{-1}$, 1562 reflections measured ($R(\text{int}) = 0.0812$), 473 unique, 392 with $I > 2\sigma(I)$ and final R values $R1 = 0.0677$ ($I > 2\sigma(I)$); $wR2 = 0.1541$ (all data). Further details of the crystal structure investigation for compounds 1 and 2 can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository numbers CSD 421419 and 421420.

Acknowledgments

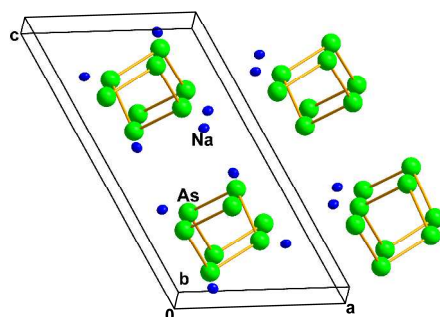
This work was supported by the Deutsche Forschungsgemeinschaft (DFG).

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Received: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

Entry for the Table of Contents

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Binary and ternary Zintl anions

Susanne Burtzloff, Małgorzata Holyńska, and Stefanie Dehnen*

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Synthesis and crystal structures of K_2SnAs_2 and a new modification of NaAs

Keywords: Zintl phases / Crystal structure / Binary Anions / Pnicogenido Stannates