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$NaSn_2$: A Novel Binary Zintl Phase with 2D Polyanions of Realgar-Type Units $[Sn_8]^{4-}$

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$NaSn_2$, obtained from the reaction of stoichiometric amounts of the elements, crystallizes in a new structure type, in which two-dimensional polyanions are separated by Na^+ cations. The tin framework is made up of Realgar-type Sn_8 units. The density of states obtained from the TB-LMTO-ASA calculations with the implementation of the electron localization function (ELF) reveals that $NaSn_2$ has all characteristics of a Zintl phase. Thus, the title compound can be written as $(Na^+)_4\,{}^{2}_{\infty}[Sn_8{}^{4-}]$. $NaSn_2$ dissolves readily in ethylenediamine, under the formation of a reddish brown solution indicative of the presence of $[Sn_9]^{4-}$ anions.

The phase $NaSn_2$ detected by thermal analysis in 1928[1] played a key role in the discovery of the first Zintl anion $[Sn_9]^{4-}$ [2] isolated from solution, which was structurally characterized by Kummer et al.[3] Therefore, in the Na/Sn phase diagram the composition $NaSn_2$ was often regarded as $NaSn_{2.25}$ (Na_4Sn_9)[2] which applies for the other alkali metal stannides $ASn_{2.25}$ ($A = K$, Rb, and Cs).[4] However, with Na_7Sn_{12} ($\sim NaSn_{1.7}$)[5] and Na_5Sn_{13} ($\sim NaSn_{2.6}$),[6] two compounds with a Na/Sn ratio close to 1:2 have been isolated.

Depending on the type of the alkali metal and the atomic ratio A/Sn, the dimensionality of the tin network can vary from 0 to 3D, and the Sn−Sn bonding reaches from localized two-electron−two-center (2e−2c) bonds to purely metallic bonding. In the Na/Sn system, the zero-dimensional tin framework is observed for the compounds Na_4Sn[7] and $Na_{15}Sn_4$[8] containing isolated Sn atoms, Na_9Sn_4[8] with dimeric Sn_2 units, and β-NaSn[9] with tetrahedral $[Sn_4]^{4-}$ anions. A two-dimensional tin network is found for the compound Na_7Sn_{12} as well as for the title compound $NaSn_2$, both of which contain two-dimensional polyanions ${}^{2}_{\infty}[Sn_{12}{}^{7-}]$ and ${}^{2}_{\infty}[Sn_8{}^{4-}]$, respectively, which are separated by layers of sodium cations. Finally, a three-dimensional tin network is found from the Na_5Sn_{13} compound. According to the Zintl concept, the valence electrons in the Na/Sn system are assigned to the tin atoms and are localized either in two-electron−two-center (2e−2c) bonds between two tin atoms or as lone pairs at the tin atoms. The 8-N rule of the concept of Zintl, Klemm, and Busmann[10,11] allows a prediction of the existence of Zintl phases. One of the most famous Zintl anions is the tetrahedral anion $[Sn_4],^{4-}$ observed in β-NaSn, $A_{52}Sn_{82}$ ($A = K$, Cs),[12] and $A_{12}Sn_{17}$ (K, Rb, Cs),[13] where it is accompanied in the latter by nido-type $[Sn_9]^{4-}$ clusters. Solely nine-atom clusters are observed in A_4Sn_9 phases for $A = K$, Rb, Cs.[4,14]

$[Sn_9]^{4-}$ anions can also be stabilized in solution by solvents such as ethylenediamine or liquid ammonia and by complexation of the Na^+ counterions with 2,2,2-crypt(4,7,13,16,21,24-hexaoxa-1,10-diazobicyclo[8,8,8]hexacosane).[15,16] The formation of the homopolyatomic anion $Sn_9{}^{4-}$ which is red-brown in solution does not necessarily require an exact and pure nominal composition of the starting material. For example, in solutions of alloys such as LiSn, $LiSn_2$, $NaSn_4$, Na_4Sn_9, $NaSn_2$ and NaSn in en or NH_3, the $[Sn_9]^{4-}$ anion can be detected by ^{119}Sn NMR spectroscopy,[17] or in the synthesis of $Na_4Sn_9(en)_{6-8}$ by Kummer et al.,[3] a Na/Sn ratio between 2:4 and 2:5 was used for the preparation of the alloy. Although $[Sn_9]^{4-}$ anion exists in solution for the complete series of the alkali metals (Li to Cs),[17] in contrast no solid phases A_4Sn_9 have been obtained so far for $A = $ Li and Na.

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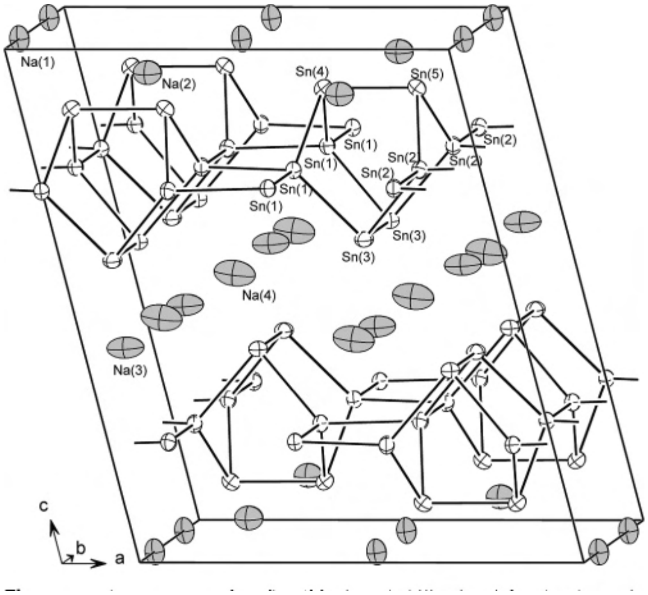

Figure 1. The structure of $NaSn_2$ (90% probability level for the thermal ellipsoids). Solid lines: Sn−Sn contacts between 2.833(1) and 2.975(2) Å.

The structure of $NaSn_2$ was determined by single-crystal X-ray diffraction. Shiny single crystals were obtained from the stoichiometric reaction of Na with Sn.[18] They crystallize in a monoclinic unit cell, space group $C2/m$, with $Z = 16$.[19] The X-ray powder diagram of the crude product shows the presence of two impurities, namely $NaSn_5$[20] and Sn. The structure of the novel compound $NaSn_2$ consists of two-dimensional Sn-polyanions, which are stacked up along the *c* direction (Figure 1). The Na cations separate these sheets of two-dimensional polyanions. The tin framework is formed by five crystallographically independent Sn atoms, which form five-membered rings and are connected along the *b* direction, thereby forming empty channels. The channels are connected along *a* to form a two-dimensional net. As a consequence, the structure contains the same number of tri- and tetracoordinated (3b and 4b) tin atoms. Thus, the formula of the new Zintl phase $NaSn_2$ can be written as $(Na^+)_4[(3b)\text{-}Sn^-]_4[(4b)Sn^0]_4$. The bonding Sn−Sn distances in the polyanion vary between 2.833(1) and 2.975(2) Å; the shortest Na−Sn and Na−Na distances are 3.121(3) and 3.42(1) Å, respectively, and are in agreement with distances found in other binary systems. The (3b)Sn−(4b)Sn−(3b)Sn angles within the Sn_8 unit are very close to the ideal tetrahedral angle with values of 108.09(2)° and 107.76(2)° for Sn(3)−Sn(2)−Sn(5) and Sn(3)−Sn(1)−Sn(4), respectively.

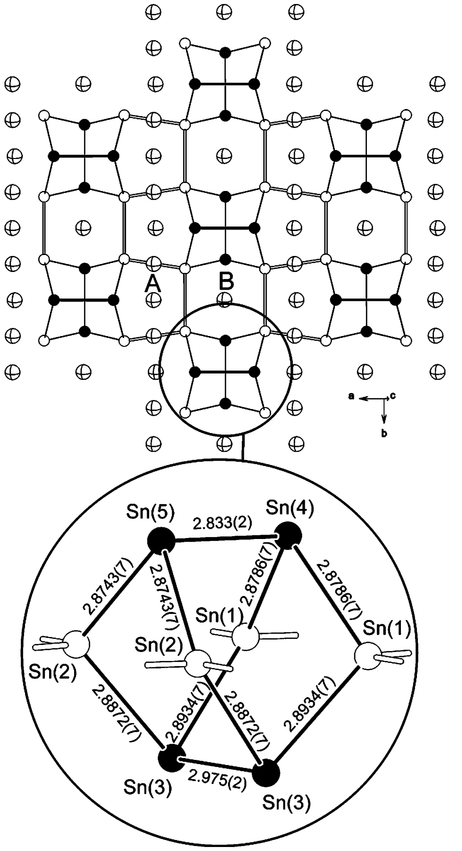

Figure 2. The tin framework of the ${}^{2}_{\infty}[Sn_8{}^{4-}]$ polyanion with one layer of Na cations (cross), in (001) projection. Dark and white circles denote (3b)-Sn and (4b)-Sn atoms, respectively. The Sn_8 units are drawn with bold lines, and the connection between the Sn_8 units is drawn with lighter lines. A and B indicate the five- and six-membered rings, respectively. Below: an isolated Sn_8 unit, distances are given in ångstroms.

The polyanionic ${}^{2}_{\infty}[Sn_8{}^{4-}]$ tin framework arises from the connection of $[Sn_8]^{4-}$ units, which are linked in two directions by the tetracoordinated Sn atoms (Figure 2). Each $[Sn_8]^{4-}$ unit, formed by both tetra- and tri-coordinated Sn atoms, is connected to six others units by eight external bonds. Thus, the formation of two kinds of rings is observed in the *ab* plane: a five-membered ring A with an envelope and a six-membered ring B with an armchair conformation. Similar eight-atoms units are also found in the mineral Realgar, β-As_4S_4,[21] and in Hittorf's phosphorus ${}_{\infty}[-P_8-P_2-P_9-P_2-]$[22] with $[P_8]$ units. Indeed, the (4b) and (3b)Sn atoms take the positions of the S and the As atoms in β-As_4S_4. In the compounds Na_7Sn_{12} and Na_5Sn_{13}, the tin frameworks contain structurally related units of 9 tin atoms which show

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(18) Details of the synthesis follow: $NaSn_2$ was synthesized by reacting stoichiometric amounts of pure elements in a niobium container which was closed by arc-welding under argon and transferred to a quartz tube. The mixture was heated at 500 °C for 100 h and then slowly cooled to 275 °C at the rate of 3 °C/h. This temperature was maintained for 2 days and then slowly cooled (6 °C/h) to room temperature. Single crystals of $NaSn_2$ had metallic luster.

(19) Details of the structure determination follow: A shiny single crystal was sealed in a capillary. X-ray data were collected at 150 K on a Enraf-Nonius KappaCCD at the window of a rotating anode (Nonius, FR591) and graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods and refined by least-squares with SHELX-97.[19a] Crystal data include the following: monoclinic, space group $C2/m$, $a = 13.3916(3)$ Å, $b = 6.88541(2)$ Å, $c = 15.4889(4)$ Å, $\beta = 102.529(2)°$, $V = 1387.83(6)$ Å^3; $Z = 16$; $\mu = 14.222$ cm^{-1}; $\rho_{calcd} = 4.985$ g cm^{-3}. The final refinement of all atoms with anisotropic displacement parameters converged to R_1/wR_2 $(I \geq 2\sigma_I) = 0.036/0.086$ and R_1/wR_2 (all data) $= 0.037/0.086$ for 1721 reflections and 63 variables; GOF $= 1.20$. The presence of residual electron density (5 e/Å^3 at 1.48 Å from Na(2)) is probably due to some Na disorder. No superstructure was observed, but diffuse scattering contributions are present, indicating incommensurable behavior. (a) Sheldrick, G. M. *SHELX-97 Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1997.

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the same connectivity pattern as observed in As_4S_5[23] and in Hittorf's phosphorus.

So far, isolated $[Sn_8]^{12-}$ units which are isoelectronic with the Realgar-type structure have not been described in the literature. The compounds $A_4Li_2Sn_8$ (A = K, Rb)[24] which contain isolated cluster anions of 8 tin atoms, $[Sn_8]^{6-}$, form square prismatic arachno clusters.

The LMTO density of states plot[25] of $NaSn_2$ shows a small gap of only 0.2 eV around the Fermi level which is indicative of semiconducting behavior. Bond analysis using the electron localization function (ELF)[26] has recently been used successfully for bond analyses of other binary stannides, for example, semiconducting Na_7Sn_{12}[5] and K_6Sn_{25}[27] and metallic $SrSn_4$.[28] For $NaSn_2$, ELF shows strong covalent contributions for all nearest Sn−Sn contacts (see in Figure 3; localization regions ①, ②, ③, ⑤, and ⑧) and the presence of lone pairs at the (3b)Sn atoms (lone pair regions ④, ⑥, and ⑦). The bond attractors (ELF maxima) are not always located on the bond vector, but are shifted, as can be seen by region ③ of the 2D diagram in Figure 3b. Due to additional repulsion, the shift is even more pronounced in an all-electron calculation (Figure 3d−f) as compared to the valence-electron calculation (Figure 3a−c). Interestingly, the two bond regions ⑤ and ⑧ between the tricoordinated atoms Sn(4)−Sn(5) and Sn(3)−Sn(3), respectively, are different. The larger area ⑤ corresponds to the shorter contact and most probably originates from different Na/Sn coordinations and therefore from a more efficient charge compensation of the 3-fold bonded $Sn(4)^-$ and $Sn(5)^-$ anions. For Sn(3), there are only two short Na−Sn distances ($d \leq 3.23$ Å), whereas for Sn(4)/Sn(5) there are three of them ($d \leq 3.13$ Å (2×) and 3.39 Å). All other Na−Sn contacts are longer than 3.5 Å. A 2D view through the Sn(2)−Sn(3) bond vector in the *ac* plane shows that there are direct contacts between the lone pairs at the Sn(3) atoms without Na cations between them (Figure 3b,e).

It has been shown that the phase $NaSn_2$ observed for the first time in 1928 by thermal analysis does not correspond to Na_4Sn_9, although the phases AE_2 and A_2E_3 with A = K, Rb, Cs and E = Si−Pb were identified as A_4M_9 and $A_{12}M_{17}$, respectively. The title compound represents a novel structure type containing two-dimensional Sn polyanions. Dissolution of this phase in ethylenediamine results in a reddish brown solution,[29] indicative of the presence of the polyanion $[Sn_9]^{4-}$. The formation of soluble Zintl anions originates rather from an oxidation of $NaSn_2$, $^9/_4Sn_8{}^{4-} \rightarrow 2[Sn_9]^{4-} + 1e^-$, than from a phase which contains preformed clusters.

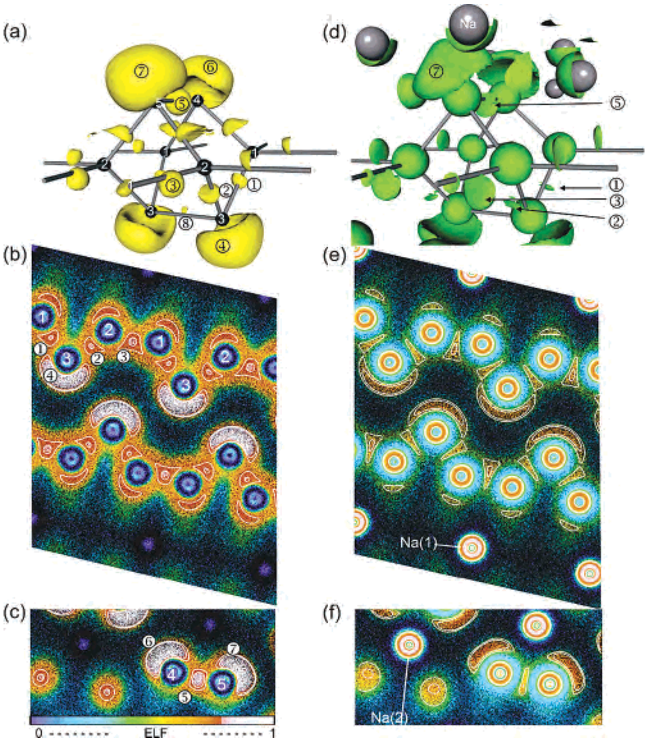

Figure 3. LMTO-ELF representation of $NaSn_2$. (a−c) Valence ELF and (d−f) all-electron calculations. (a) 3D plot with ELF = 0.75 of a Realgar-type unit, (b) 2D plot through the Sn(1)−Sn(3) bond vector in the *ac* plane highlighting contour lines ELF = 0.75 and 0.80, (c) 2D plot in the plane of Sn(4) and Sn(5) atoms and in the *ac* plane with ELF = 0.75 and 0.80. (d) 3D ELF = 0.50, structure detail as in part a including Na atoms, green spheres at atom positions reflect core shells of Sn and Na atoms. For parts e and f, all-electron ELF plots as in parts b and c, respectively. The color of each pixel corresponds to a specific ELF value as indicated in the color bar at the bottom of part c.

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Supporting Information Available: Tables of data collection and refinement parameters, positional and anisotropic displacement parameters, distances, and angles, as well as a density-of-states plot. X-ray crystallographic files in CIF format. This material is available free of charge via Internet at http://pubs.acs.org.

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(29) A 100 mg portion of $NaSn_2$ ($NaSn_2$, $NaSn_5$, and Sn metal are identified by X-ray powder diffraction) dissolves in en, and the solution turns to red-brown color, with some particles not soluble.