Inorg. Chem. **2003**, *42*, 5474–5476

Inorganic Chemistry
Communication

Na_7Sn_{12}: A Binary Zintl Phase with a Two-Dimensional Covalently Bonded Tin Framework

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Received May 6, 2003

Na_7Sn_{12} was synthesized by quenching of stoichiometric amounts of the elements (700 °C) in a sealed niobium ampule and further thermal treatment at 270 °C for 40 days. Single crystals of Na_7Sn_{12} were obtained from a mixture with the composition Na_6SrSn_{16}. The structure of Na_7Sn_{12} consists of two-dimensional polyanions $^{2}_{\infty}[\mathrm{Sn}_{12}{}^{7-}]$, which are separated by Na atoms. Bonding Sn–Sn contacts in the polyanion vary between 2.827(2) and 3.088(2) Å. Crystal data: monoclinic, *P*2/*n*, $Z = 4$, $a = 13.375(3)$ Å, $b = 9.239(2)$ Å, $c = 17.976(4)$ Å, $\gamma = 90.15(3)°$, $V = 2243.0(8)$ Å^3, $\mu = 13.22$ mm^{-1}, $d_{\mathrm{calc}} = 4.694$ g cm^{-3}, R1(*F*) = 6.1% (for all reflections). Extended-Hückel tight-binding calculations with the implementation the *electron localization function* (ELF) reveal that Na_7Sn_{12} can be viewed as an intermetallic compound with exclusively localized bonding and nonbonding regions as expected from the 8 – *N* rule. Thus Na_7Sn_{12} is a Zintl phase with the formula $(\mathrm{Na}^+)_7[(2b)\mathrm{Sn}^{2-}]_1[(3b)\mathrm{Sn}^-]_5[(4b)\mathrm{Sn}^0]_6$.

Novel allotropes of carbon group elements show intriguing physical properties, and the recent discovery of several new modifications of carbon lead even to the opening of new research fields. *allo*-Si[1] and *allo*-Ge[2] were obtained by oxidative removal of the alkali metals from the Zintl phases Li_3NaSi_6 and Li_7Ge_{12}, respectively, and recently we proposed a novel modification of Ge constructed from nine-atom clusters.[3] The educts Li_3NaSi_6 and Li_7Ge_{12} used for the topotactic formation of *allo*-Si and *allo*-Ge contain the two-dimensional polyanions $^{2}_{\infty}[\mathrm{Si}_6{}^{4-}]$ and $^{2}_{\infty}[\mathrm{Ge}_{12}{}^{7-}]$, respectively. During our investigations of binary alkali metal and alkaline-earth metal stannides we were now able to establish the structure of the corresponding stannide Na_7Sn_{12} (Table 1), which contains the two-dimensional polyanion $^{2}_{\infty}[\mathrm{Sn}_{12}{}^{7-}]$. This makes the title compound interesting with respect to the formation of novel element modifications of Sn.

Table 1. Data Collection and Refinement Details for Na_7Sn_{12}

chemical formula	Na_7Sn_{12}
fw	1585.2 g/mol
space group	*P*2/*n* (No. 13)
Z	4
unit cell parameters	$a = 13.375(3)$ Å
	$b = 9.329(2)$ Å
	$c = 17.976(4)$ Å
	$\gamma = 90.15(3)°$
volume	2243.0(8) Å^3
temperature	293(2) K
density (calculated)	4.694 g/cm^3
μ(Mo Kα)	13.220 mm^{-1}
λ(Mo Kα)	0.71073 Å
R indices (all data)	R1 = 0.061, wR2 = 0.113[a,b]

[a] $\mathrm{R1} = \sum||F_o| - |F_c|/\sum|F_o|$; $\mathrm{wR2} = [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]]^{1/2}$. [b] $w = 1/[\sigma^2 F_o{}^2 + 151.11P]$, $P = (F_o{}^2 + 2F_c{}^2)/3$.

The combination of two main-group metals which have a large difference in their electronegativities leads in the case of the alkali metals A and tin to an astonishing large number of compounds. Solely in dependency on the kind of alkali metal and the atomic ratio A:Sn a large variety of chemical bond types reaching from localized two-electron two-center (2e−2c) bonds to purely metallic bonds are established. Some outstanding examples are the Zintl-phase β-NaSn (Na_4Sn_4), which contains $[\mathrm{Sn}_4{}^{4-}]$ units. Compounds of the compositions K_4Sn_9 and $Rb_{12}Sn_{17}$ contain $[\mathrm{Sn}_9{}^{4-}]$ clusters. They are valence compounds if we regard the $[\mathrm{Sn}_9{}^{4-}]$ anion as an electronically balanced nido-type cluster. $K_{6+x}Sn_{25}$ and K_8Sn_{46-x} show a three-dimensional covalent framework of larger tin polyhedra, which are filled with A atoms. For $x = 0$ they do not obey the $8 - N$ rule, but show an electron deficiency and an electron excess, respectively. In Na_5Sn_{13} tin atoms are also predominantly connected by 2e−2c bonds; however, one long Sn−Sn contact of 3.6 Å has to be considered as a bonding one in order to have a Zintl phase. In $NaSn_5$ we finally see structure motifs of the covalently bonded α-Sn and the metallic β-Sn. They occur in the form of fragments of pentagondodecahedral units of 4-fold bonded (4b) atoms and interatomic distances as in α-Sn, besides quadratic nets of 5-fold bonded atoms with atom−atom separations as in β-Sn.[4,5]

Single crystals of Na_7Sn_{12} were obtained by quenching stoichiometric amounts of the elements from 700 °C and

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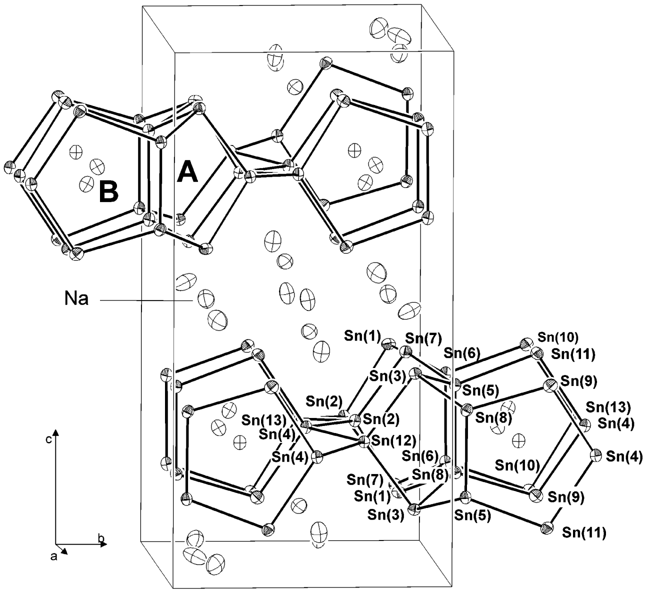

Figure 1. Structure of Na_7Sn_{12} (50% probability level for the thermal ellipsoids) with outlined unit cell: solid lines represent Sn−Sn contacts between 2.827(2) and 3.088(2) Å. A and B denote the characteristic channels in the two-dimensional $^{2}_{\infty}[Sn_{12}{}^{7-}]$ polyanion

thermal treatment of the product at 270 °C for 40 days in a sealed niobium ampule.[6] The diffraction pattern of the powdered product compares well with the calculated diagram for Na_7Sn_{12} from the single-crystal structure determination. In addition a small amount of tin was detectable. A DTA of the product shows a small endothermic effect at 320 °C followed by a pronounced one at 330 °C during the first heating. Since the assignment of the decomposition points does not correspond to $NaSn_2$ and $NaSn_3$ which are expected from the phase diagram,[7,8] Na_7Sn_{12} represents a novel phase in the system Na−Sn.

The structure of the new compound Na_7Sn_{12} consists of two-dimensional polyanions, which are stacked along *c* (Figure 1). The Na cations separate these layers and are intercalated in the polyanion (Figure 1, channel B). There are 13 independent Sn positions. Two of them are located on a 2-fold rotation axis (Sn(12) and Sn(13) at 2f and 2e Wyckoff sites, respectively) leading to the composition Na_7Sn_{12}. The short Sn−Sn contacts in the polyanion vary between 2.827(2) and 3.088(2) Å. Interpreting these short contacts as single bonds, different valancies and therefore charges for the Sn atoms result. The formula Na_7Sn_{12} can be rewritten as $(Na^+)_7[(2b)Sn^{2-}]_1[(3b)Sn^-]_5[(4b)Sn^0]_6$ (2b and 3b denote 2- and 3-fold bonded atoms, respectively) assuming a complete charge transfer from Na to the tin atoms. Thus Na_7Sn_{12} is an electron precise compound. The shortest nonbonding Sn−Sn distance is 4.119(2) Å.

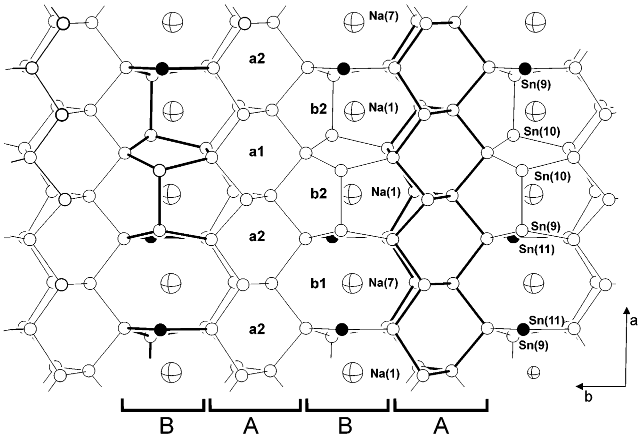

Figure 2. Top view of the $^{2}_{\infty}[Sn_{12}{}^{7-}]$ polyanion with intercalated Na ions. a1, a2 and b1, b2 denote polyhedra, which build up channels A and B, respectively. Light gray, dark gray, and black circles denote (4b)Sn, (3b)-Sn, and (2b)Sn atoms, respectively. To the left: The five-membered rings of Sn atoms form channel B (Figure 1), and interconnections between the rings are highlighted. To the right: Cages which form channel A are emphasized.

The structure of the complex polyanion $^{2}_{\infty}[Sn_{12}{}^{7-}]$ can be easily rationalized by a partition into channels which run parallel to the *a* direction. They are marked in Figure 1 with capitals A and B. For a detailed discussion a top view of the polyanion is given in Figure 2. Channel A consists of two slightly different cages a1 and a2, which are built up by five (4b) Sn and four (3b) Sn atoms. Each cage has two corrugated five-membered Sn rings and two six-membered rings in an armchair conformation comparable to those found in Hittorf's phosphorus and arsenic sulfide. The condensation of two neighboring cages sharing three Sn atoms leads to channel A. Additional Sn atoms (Sn(9), Sn(10), and Sn(11); Figure 2) link the A-type channels to a two-dimensional anion. Consequently, two larger polyhedra (b1 and b2) are formed which are able to incorporate the Na cations Na(7) and Na(1), respectively. Both polyhedra have in common that two opposite sites are nearly planar five-membered Sn rings (mean deviations from idealized planes through five Sn atoms are 0.126 and 0.151 Å, respectively). Therefore, in the view of the projection in Figure 1 channel B occurs as a distorted pentagonal channel. In polyhedron b2 the opposite five-membered rings are linked by a bond between Sn(9) and Sn(10) (Figure 2). In contrast, there is no Sn−Sn bond in polyhedron b1, but a 2-fold bonded Sn(11).

Extended-Hückel tight-binding calculations were carried out with the implementation of real space analysis routines.[9] The electron localization function (ELF) that was originally introduced for the deduction of the shell structure of atoms from the electron density[10] allows the topographical analysis of the electron density distribution of molecules and solids. ELF values are scaled between 1 and 0 with the meaning

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(6) X-ray diffraction data were collected on a two-circle Stoe IPDS II diffractometer at 293 K from a single crystal (0.3 × 0.05 × 0.02 mm^3) with monochromated Mo Kα radiation. The structure of Na_7Sn_{12} shows a great similarity to Li_7Ge_{12}, which was solved in the orthorhombic space group $Pmn2_1$. However, Na_7Sn_{12} shows a significant deviation from this symmetry.

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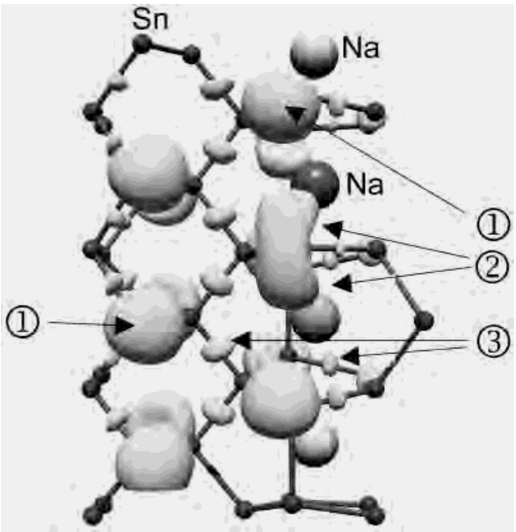

Figure 3. 3D-isosurface of ELF with ELF = 0.77 of a structure detail of the polyanion. Areas of type ① designate nonbonding electron pairs at (3b)-Sn atoms, type ② reflects two nonbonding electron pairs at (2b)Sn atoms, and ③ various types of covalent Sn−Sn single bonds.

that high ELF values and local ELF maxima correspond to areas and centers of localized electrons, respectively. Low ELF values are used to define the spatial area around these maxima. As a consequence the partition of space into areas of high electron localization is possible and the chemist's intuitive view of bonding and nonbonding electron pairs and their three-dimensional shape or in other words the spatial localization of electrons becomes visible.[11] In Figure 3 localized 2e−2c Sn−Sn bonds ③ and one lone pair ① at (3b)Sn atoms, as well as two neighboring lone pairs ② at (2b)Sn atoms are evident. Thus Na_7Sn_{12} can be viewed as an intermetallic compound with exclusively localized bonding and nonbonding regions as expected from the $8 - N$ rule.

The noticeable characteristics of the polyanion $^{2}_{\infty}[Sn_{12}{}^{7-}]$ are the channels A and B parallel to *a* (Figure 1). Channel B is built up of Sn pentagons. A comparable arrangement of tetrel rings is found in $Li_{12}Si_7$ where columns of isolated parallel pentagons separated by Li are observed[12] and in Li_2Sn_5 where pentagonal channels of Sn atoms are a substructure of a three-dimensional network.[13] Each cage a1 and a2 in part A (Figure 2) consists of nine Sn atoms. Isolated cages with the same connectivity of atoms were reported for the compound As_4S_5;[14] the same structure motif is also present in Hittorf's phosphorus. The condensation of those cages to A-type strings is also realized in Li_3NaSi_6, KSi_3As_3, and $GeAs_2$.[12,15,16] Both kinds of channels are also observed in Na_5Sn_{13}.[17] According to the lower content of sodium in Na_5Sn_{13} compared to the title compound the channels are part of a three-dimensional network. In addition the B-type channel (Figure 2) differs slightly, and there are no two-bonded Sn atoms in Na_5Sn_{13}.

Removal of Na from Na_7Sn_{12} and oxidation of the polyanion at room temperature leads to the formation of β-Sn. Further investigations of topochemical reactions are under study.

Acknowledgment. The authors thank the Fonds der Chemischen Industrie for financial support.

Supporting Information Available: Table of data collection and refinement details, positional and thermal parameters, anisotropic displacement parameters, and important distances as well as an 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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