

In Search of Benzene-like Sn_6^{6-} : Synthesis of Na_4CaSn_6 with Interconnected Cyclohexane-like Sn_6^{6-}

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The title compound was synthesized in an attempt to produce stacked benzene-like Sn_6^{6-} rings separated by alkaline-earth cations in analogy with the recently reported stacks of aromatic cyclopentadienyl-like Sn_5^{6-} in Na_8BaSn_6 (in addition to isolated Sn^{4-} anions). The resulting compound, synthesized from a stoichiometric mixture of the elements at high temperature, has the “correct” stoichiometry with six tin atoms and six positive charges. However, the rings of Sn_6^{6-} are puckered into chair-type cyclohexanes that are interconnected into isolated cylindrical tubes stuffed with Ca^{2+} between the rings. Such tubes, if fused to each other, form the hexagonal diamond structure. The new compound is electronically balanced according to magnetic and four-probe resistivity measurements. Reported are also the synthesis and properties of $\text{Na}_{10}\text{EuSn}_{12}$ and $\text{Na}_{10}\text{YbSn}_{12}$ which are isostructural with the known $\text{Na}_{10}\text{CaSn}_{12}$.

Introduction

Historically, the concept of aromaticity has been associated with organic compounds.¹ Its origin is in the failure to rationalize bonding in some cyclic planar molecules as localized 2-center–2-electron bonds because of the fewer bonding pairs of electrons (and bonding orbitals) than interatomic contacts. The only option, therefore, is the concept of delocalized bonding where the electrons are delocalized over the whole ring. Such planar aromaticity is π -aromaticity where the delocalized electrons occupy π -type molecular orbitals that are above the already occupied σ -manifold of orbitals. The concept of delocalization can be extended further into three-dimensional systems such as the deltahedral boranes and Zintl anions where all bonding electrons are delocalized (i.e., without underlying σ -manifold with 2-center–2-electron bonds), and such systems can be viewed as three-dimensional or σ -aromaticity.

The planar or π -aromaticity has been identified in fragments made of the heavier analogues of the carbon group, as well as of elements of other main groups. However, the synthesis and structural characterization of such species is extremely challenging, and as a result, only very few are known. Some of the first examples of group 13 are the

tetrameric dianions of Al_4^{2-} , Ga_4^{2-} , and In_4^{2-} experimentally detected in gas phase that are both isostructural and isoelectronic with the cyclobutadienium dication, $\text{C}_4\text{H}_4^{2+}$.² The ones known in group 14 are the triangular Si_3^{2-} and Sn_3^{2-} in Ba_2NiSi_3 and SrSn_3 , respectively; they are similarly isostructural and isoelectronic with the cyclopropenium cation, C_3H_3^+ .^{3,4} The triangles of silicon in Ba_2NiSi_3 are stacked on top of each other in an eclipsed mode and are separated by the Ni atoms forming metallocene-like columns. The cyclopentadienyl anion, C_5H_5^- , has also its isostructural and isoelectronic analogues among the heavier elements of this group such as Si_5^{6-} in Li_8MgSi_6 ⁵ and the more recently characterized Sn_5^{6-} and Pb_5^{6-} in isostructural Na_8BaSn_6 (and Na_8EuSn_6) and Na_8BaPb_6 , respectively.^{6,7} (Despite its analogous stoichiometry, Li_8MgSi_6 differs from the Sn and Pb compounds in the positioning of the alkali and alkaline-earth elements.⁵) The flat pentagonal rings in these compounds are also stacked eclipsed on top of each other. Also similar to Ba_2NiSi_3 , the rings are separated by cations in the stacks,

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such as lithium in Li_8MgSi_6 and alkaline-earth (or rare-earth) in the remaining compounds, and form infinite columns of metallocene-like units. Clearly, these pentagonal and triangular species exist because of the stabilizing effect of the coordinating metal atom between them (i.e., Li, Ba, Eu, and Ni). Subsequent further exploration of the Sn system by changing the alkali metal to lithium led to a series of compounds $\text{Li}_{9-x}\text{EuSn}_{6+x}$, $\text{Li}_{9-x}\text{CaSn}_{6+x}$, $\text{Li}_5\text{Ca}_7\text{Sn}_{11}$, and $\text{Li}_6\text{Eu}_5\text{Sn}_9$ with the same columns of stacked Sn_5^{6-} rings separated by the corresponding alkaline- or rare-earth cations.⁶ It should be mentioned that, in addition to the columns, all tin compounds contain a second tin motif, such as isolated atoms, bent trimers, flat hexamers, and infinite and flat zigzag chains.^{6,7}

Finally, nearly-planar hexagonal formations of Si and Ge have been also reported: Si_6^{10-} and Ge_6^{10-} in $\text{Li}_2\text{Ba}_4\text{Si}_6$ and $\text{Li}_2\text{Ba}_4\text{Ge}_6$, respectively.⁸ However, these species are only geometrically similar to benzene (i.e., they are nearly flat hexagonal rings), but electronically they differ by 4 electrons. These additional electrons occupy the two degenerate low-lying π^* -orbitals, and the overall π -bond order drops to 1/6 per bond. The hexagons are again coordinated on both sides by barium, exactly as in the triangles and pentagons discussed above, but are not stacked in columns.

On the basis of the above examples of solid state structures containing aromatic anions, one can make the following general empirical deductions. The aromatic anions tend to stack eclipsed to each other and form columns. The structures typically contain two types of cations which, in addition to providing electrons, have different functions. One of them coordinates to the aromatic anions and separates them within the columns. The second-type cation separates the columns. Following these concepts, we attempted the rational synthesis of benzene-like Sn_6^{6-} anions in Na_4CaSn_6 where the rings would be stacked eclipsed in columns and separated by the calcium cations. A compound with the proposed stoichiometry and stacked eclipsed hexagonal rings of tin was successfully synthesized. However, the rings are puckered as in chairlike cyclohexane and are close enough to form inter-ring bonds. Reported here are the synthesis and characterization of the new compound, Na_4CaSn_6 , as well as of $\text{Na}_{10}\text{EuSn}_{12}$ and $\text{Na}_{10}\text{YbSn}_{12}$, which are isostructural with $\text{Na}_{10}\text{CaSn}_{12}$.⁹ The latter two compounds resulted from attempts to synthesize the Eu and Yb analogues of Na_4CaSn_6 .

Experimental Section

Synthesis. All manipulations were carried out in an argon-filled glovebox with a moisture level below 1 ppm (vol). The elements Ca (granules, Strem, 99.5%) and Yb (ingot, Acros, 99.9%) were used as received, while the surfaces of Eu (ingot, Ames Laboratory DOE, 99.9%) and Na (ingot, Alfa, 99.9%) were cleaned with a scalpel before use. In a typical synthesis, a mixture of the elements is placed in a niobium tube that is then sealed by arc-welding. The tube is in turn jacketed in a silica ampule that is then flame-sealed under vacuum.

Table 1. Selected Data Collection and Refinement Parameters for Na_4CaSn_6

formula	Na_4CaSn_6
fw	844.18
space group, <i>Z</i>	$P6_3/mmc$, 2
<i>a</i>	10.0486(3) Å
<i>c</i>	7.1375(3) Å
<i>V</i>	624.15(4) Å ³
radiation, λ	Mo K α , 0.710 73 Å
temp	20 °C
ρ_{calcd}	4.492 g cm ⁻³
μ	12.309 cm ⁻¹
R1/wR2, ^a $I \geq 2\sigma I$	2.28/3.90%
R1/wR2, ^a all data	2.62/4.01%

$$^a \text{R1} = \frac{[\sum ||F_o| - |F_c||] / \sum |F_o|}{\sum w[(F_o)^2 - (F_c)^2]^2} / \sum w(F_o)^2]^{1/2}; \text{wR2} = \frac{\{[\sum w[(F_o)^2 - (F_c)^2]^2] / [\sum w(F_o)^2]\}^{1/2}}{w} = [\sigma^2(F_o)^2 + 1.1782P]^{-1}, \text{ where } P = [(F_o)^2 + 2(F_c)^2] / 3.$$

The initial synthesis of Na_4CaSn_6 from the stoichiometric mixture of the elements (heated at 760 °C for 2 weeks and then slowly cooled to room temperature with a rate of 0.5 °C/min) did not produce the compound as a single phase but mixed with impurity phases of NaSn and CaSn. The synthesis was later refined by testing variety of different temperature profiles, as well as slightly nonstoichiometric mixtures. A pure phase, according to powder X-ray diffraction (Enraf-Nonius Guinier camera under vacuum, Cu K α_1 radiation, $\lambda = 1.540562$ Å), was obtained from a stoichiometric mixture heated at 800 °C for 1 h, then quenched in liquid nitrogen, and finally annealed at 200 °C for 1 week.

The attempts to synthesize the corresponding Sr, Eu, and Yb compounds were unsuccessful. Instead, the reactions produced the known $\text{Na}_{10}\text{SrSn}_{12}$ ⁹ and its isostructural new compounds $\text{Na}_{10}\text{EuSn}_{12}$ and $\text{Na}_{10}\text{YbSn}_{12}$, in addition to impurity-level amounts of binary phases such as NaSn, SrSn, EuSn, as well as elemental Sn. The synthesis of $\text{Na}_{10}(\text{RE})\text{Sn}_{12}$ was later refined, and pure phases were achieved by heating stoichiometric mixtures at 860 °C for 2 weeks, quenching the samples in liquid nitrogen, and then annealing them at 550 °C for 2 weeks.

Structure Determination. The structures of Na_4CaSn_6 , $\text{Na}_{10}\text{EuSn}_{12}$, and $\text{Na}_{10}\text{YbSn}_{12}$ were determined by single-crystal X-ray diffraction. Single crystals (black blocks) from each compound were sealed in thin-walled glass capillaries and were checked for singularity on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). X-ray diffraction data sets were collected at room temperature ($\omega - 2\theta$ scans, $\theta_{\text{max}} = 25^\circ$). The observed extinction conditions and intensity statistics suggested the centrosymmetric space group $P6_3/mmc$ for Na_4CaSn_6 and the acentric body-centered space group $I43m$ for $\text{Na}_{10}(\text{RE})\text{Sn}_{12}$ ($a = 11.2189(3)$ and $11.1768(4)$ Å for $\text{Na}_{10}\text{EuSn}_{12}$ and $\text{Na}_{10}\text{YbSn}_{12}$, respectively). Accordingly, the structures were solved and refined in these space groups with the aid of the SHELXTL, version 5.1, software package.¹⁰ Further details for the data collection and structure refinement of Na_4CaSn_6 are given in Table 1 (the CIF files for all three compounds are available as Supporting Information).

Properties Measurements. The magnetizations of Na_4CaSn_6 , $\text{Na}_{10}\text{EuSn}_{12}$, and $\text{Na}_{10}\text{YbSn}_{12}$ were measured on a Quantum Design MPMS SQUID magnetometer at a field of 3 T over a temperature range of 10–250 K. Each sample was sealed in a quartz tube between two quartz rods that fit tightly in the tube. The data were corrected for the holder and for ion-core diamagnetism. The electrical resistivities of the three compounds were measured by the four-probe method (an in-line probe from Jandel) on pressed

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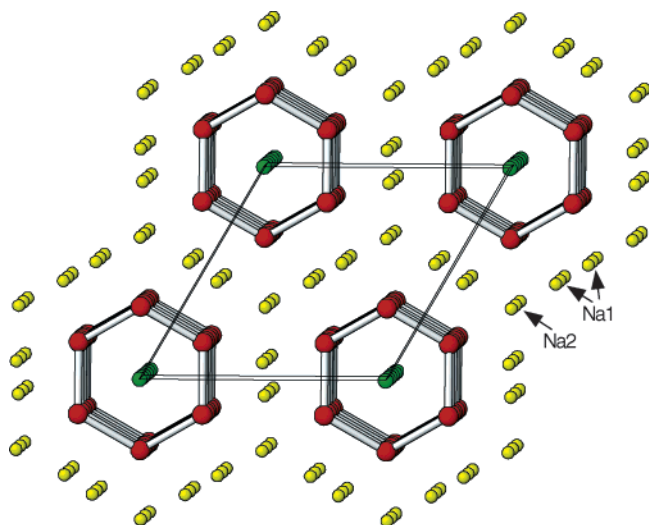


Figure 1. View of the structure of Na_4CaSn_6 along the c axis (Sn, red; Ca, green; Na, yellow). The Ca-stuffed tubes of Sn_6^{6-} are embedded in a matrix of sodium cations.

pellets (2000–3000 psi, 0.4–1.0 mm thick) over the temperature range of 222–296 K inside a cold well of a drybox.

Results

Structure Description. The anionic substructure of Na_4CaSn_6 consists of isolated tubes of tin with a repeating unit of Sn_6^{6-} (Figure 1). The tubes are “stuffed” with calcium cations and run along the c axis of the hexagonal cell. They are screened by the sodium cations, virtually embedded in their matrix. Viewed along the c axis of the hexagonal cell, as shown in Figure 1, the tubes seem to be made of (falsely) flat benzene-like hexagonal rings. In reality, however, the hexagonal rings are puckered as a chairlike cyclohexane and are interconnected as can be seen from the side view of the chain (Figure 2). The rings are stacked on top of each other in an eclipsed fashion but are puckered in opposite directions. This brings tin atoms from neighboring rings close to each other, close enough to form Sn–Sn bonds of 3.008 Å that compare well with the distance in the rings, 2.985 Å (there is only one crystallographically unique tin atom in the structure). Each ring is involved in six such inter-ring bonds, three to each neighboring ring, and the tin atoms become three-bonded. The walls of the resulting tubes are made of cyclohexane-like panels but in the boat conformation as can be seen in the side view shown in Figure 2.

The calcium cations are encapsulated inside the tin tubes, one cation between a pair of rings. Each cation is coordinated quite spherically by twelve tin atoms, six of them at 3.295 Å from Ca and the other six slightly farther at 3.586 Å. The two neighboring calcium cations within the tube are at 3.569 Å. There are two crystallographically different sodium cations. One of them, Na2, occupies a position along the 3-fold axis in the center between three tin tubes (Figure 1). Each cation is coordinated by three pairs of tin atoms (each pair forms an inter-ring bond) forming a trigonal prismatic environment with a Na2–Sn distance of 3.240 Å. Thus, each inter-ring bond in a tube is bridged on the outside by a sodium cation, and each cation “connects” three tubes. The

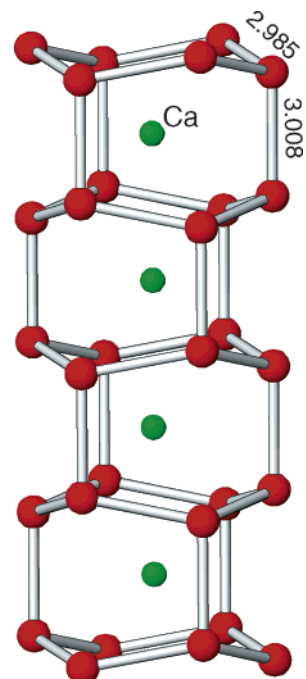


Figure 2. Side view of the Ca-stuffed tubes of $\infty^1[\text{Sn}_6^{6-}]$ made of interconnected cyclohexane-like Sn_6 units in chair conformation stacked eclipsed on top of each other. Each tin atom is three-bonded (i.e., Sn^-), and therefore each cyclohexane ring is six-bonded.

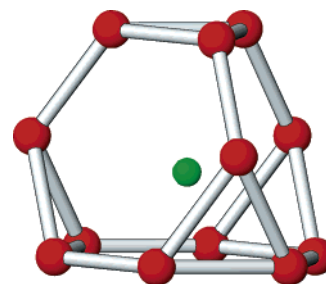


Figure 3. View of the isolated cages of 12 tin atoms (known as Friauf polyhedra) centered by an alkaline- or rare-earth cation in the isostructural $\text{Na}_{10}\text{CaSn}_{12}$, $\text{Na}_{10}\text{SrSn}_{12}$, $\text{Na}_{10}\text{EuSn}_{12}$, and $\text{Na}_{10}\text{YbSn}_{12}$. All sodium cations (not shown) are between the cages.

second type of sodium cations, Na1, cap the boatlike cyclohexagonal faces of the tube with two cations per face. In the boat conformation, the hexagons are bent along a long diagonal (Figure 2), and each of the resulting two flat trapezoid-like windows is capped by a Na1 cation with Na1–Sn distances of 3.320 and 3.624 Å, two of each kind. Each Na1 cation caps windows in two neighboring tubes and is shared between them (figure in Supporting Information).

Although the structure of $\text{Na}_{10}\text{EuSn}_{12}$ and $\text{Na}_{10}\text{YbSn}_{12}$ has already been reported for $\text{Na}_{10}\text{CaSn}_{12}$ and $\text{Na}_{10}\text{SrSn}_{12}$,⁹ a short overview is necessary for comparison and further discussion purposes. It contains isolated cages of twelve three-bonded tin atoms (Figure 3) that are centered by Ca, Sr, Eu, or Yb and are embedded in the matrix of sodium cations. The shape of the cages, often referred to as Friauf polyhedra, is that of a truncated tetrahedron. The distances in $\text{Na}_{10}\text{CaSn}_{12}$ are 2.869 and 2.963 Å for Sn–Sn, and 3.424 Å for Ca–Sn.

Properties. Room-temperature resistivities of ca. 0.015, 0.005, and 1.53 Ω cm were measured for Na_4CaSn_6 , $\text{Na}_{10}\text{EuSn}_{12}$, and $\text{Na}_{10}\text{YbSn}_{12}$, respectively. These values compare

well with other semiconducting compounds in similar intermetallic systems such as Na_8EuSn_6 (0.09 Ω cm),⁶ $\text{Ca}_{14}\text{-MnAs}_{11}$ (0.10 Ω cm),¹¹ and $\text{Sr}_{14}\text{CdSb}_{11.37}$ (0.63 Ω cm).¹² Upon a decrease of the temperature, these resistivities increase as expected for semiconductors. The calculated band gaps from the plots of $\ln(\rho)$ versus $1/T$ are ca. 0.18, 0.09, and 0.21 eV for Na_4CaSn_6 , $\text{Na}_{10}\text{EuSn}_{12}$, and $\text{Na}_{10}\text{YbSn}_{12}$, respectively.

Na_4CaSn_6 and $\text{Na}_{10}\text{YbSn}_{12}$ show temperature-independent and negative magnetic susceptibilities of $-(2.180\text{--}2.126) \times 10^{-3}$ and $-(2.832\text{--}2.466) \times 10^{-3}$ emu/mol, respectively, indicative of diamagnetic properties. As expected, $\text{Na}_{10}\text{-EuSn}_{12}$ is paramagnetic with a classical Curie–Weiss temperature dependence of the magnetic susceptibility. The data were fitted with $\chi_m = C/(T - \Theta)$ which provided $\mu_{\text{eff}} = 8.14 \mu_B$ and $\Theta = -3.87$ K (99.9% fit precision), and this is consistent with 7 unpaired electrons (the theoretical spin-only moment for Eu^{2+} is $7.94 \mu_B$). Thus, the magnetic data for the three compounds corroborate the observed semiconducting behavior from the conductivity measurements.

Discussion

The previously reported Na_8AeSn_6 compounds where Ae is an alkaline-earth (or divalent rare-earth) cation contain stacks of aromatic pentagons of Sn_5^{6-} and isolated Sn^{4-} anions, and the formula can be rationalized as $(\text{Na}^+)_8(\text{Ae}^{2+})\text{-}(\text{Sn}_5^{6-})(\text{Sn}^{4-})$.⁶ Hypothetically, if the isolated tin atom became part of the flat ring and formed an aromatic hexagon the formation would carry the same charge of $6-$ (i.e., Sn_6^{6-}). Therefore, four positive charges should be removed for an electronically balanced compound. The divalent cation cannot be removed because it plays an essential role in all observed structures with aromatic rings by coordinating to the rings in the observed stacks. Thus, the logical proposition for a compound containing benzene-like Sn_6^{6-} species would be Na_4AeSn_6 , and this was our approach to the attempted rational synthesis of the heavy-atom aromatic anions.

To our amusement, the compound that was obtained from the Na–Ca–Sn system had exactly the same stoichiometry as the proposed one, namely, Na_4CaSn_6 . The tin substructure, however, is made of tubes of interconnected cyclohexane-like rings and not isolated benzene-like Sn_6^{6-} . Nonetheless, this observed structure is very closely related to the proposed compound with stacked benzene-like rings, referred to as $\pi\text{-Na}_4\text{CaSn}_6$ hereafter, and can be viewed as being made in two steps from it. In the first step, the rings are puckered into chairlike cyclohexane species. In the second step, bonds are formed between the neighboring rings resulting in all σ -bonded tin atoms in the observed Na_4CaSn_6 , referred to as $\sigma\text{-Na}_4\text{CaSn}_6$.

The interplanar distance between the hypothetical benzene-like rings of eclipsed Sn_6^{6-} that are stacked in the hypothetical $\pi\text{-Na}_4\text{CaSn}_6$ can be easily estimated based on the Ca–Sn and Sn–Sn distances of 3.40 and 2.92 Å, respectively,

observed for the stacks of cyclopentadienyl-like rings of eclipsed Sn_5^{6-} with Ca cations between them in $\text{Li}_{9-x}\text{CaSn}_{6+x}$ and $\text{Li}_5\text{Ca}_7\text{Sn}_{11}$.⁷ This results in a distance of ca. 3.48 Å that is shorter than the shortest interplanar distance of 4.66 Å observed between pentagons of Sn_5^{6-} in any of the known compounds. This difference, of course, is the result of the larger opening of the benzene-like Sn_6^{6-} than that of the cyclopentadienyl-like Sn_5^{6-} and, at the same time, the constant Ca–Sn and Sn–Sn distances for the two species. Interestingly, the distance between the mean planes of the cyclohexane-like rings in the observed $\sigma\text{-Na}_4\text{CaSn}_6$, 3.57 Å, is very close to this calculated distance between the hypothetical benzene-like rings. This suggests that the latter are too large for sufficient separation by calcium cations and, as a result of this, they become too close to each other when stacked with calcium between them. This would, in turn, lead to relatively strong $\pi\text{-}\pi$ interactions between the rings in the stacks. The electronic structure of such a stack is characterized with relatively wide filled bands that develop from the three occupied π -molecular orbitals of the benzene rings. The character of the upper states of these bands is strongly antibonding and this leads to overall repulsion between the rings. One can make direct analogy with the well-known eclipsed stacks of d^8 square-planar platinumocyanides $[\text{Pt}(\text{CN})_4]^{2-}$ in $\text{K}_2[\text{Pt}(\text{CN})_4]$.¹³ The filled four platinum d orbitals, z^2 , xz , yz , and xy (analogous to the filled π -orbitals in Sn_6^{6-}), develop similarly filled bands that are antibonding at their high-energy states, and the overall interaction between the complexes in the stack is antibonding. The bands developed from the π -systems of the Sn_5^{6-} rings, on the other hand, are simply nonbonding and flat because of the much longer inter-ring distances in the stacks.

The distortion of the benzene rings into cyclohexanes (without overall displacement of the rings) where neighboring rings pucker in opposite directions brings pairs of tin atoms close enough to form σ -bonds. The π -system in the rings disappears by converting the low-lying π^* -orbitals to the high-energy σ^* -orbitals and high-lying π -bonding orbitals to low-energy σ -bonding orbitals. This opens a gap in the density of states that is calculated at ca. 3.5 eV (from extended Hückel calculations). Each tin atom in the resulting structure is three-bonded to other tin atoms in a trigonal pyramidal geometry with angles of 100.95 ($\times 2$) and 116.48° . This indicates that each atom also carries a lone pair of electrons. Such a coordination corresponds to a formal charge of $1-$ per tin atom (i.e., 3-bonded Sn^-), while a four-bonded tin atom with full tetrahedral coordination is neutral (i.e., 4-bonded Sn^0). Isolated cyclohexane-like rings of Sn_6 have been characterized before as stabilized by two (tol)Nb fragments coordinated at both sides of the rings (just like calcium in Na_4CaSn_6) (i.e., $[(\text{tol})\text{NbSn}_6\text{Nb}(\text{tol})]^{2-}$).¹⁴ These species were made by a reaction of $(\text{tol})_2\text{Nb}$ with an ethylenediamine solution of the Zintl phase, K_4Sn_9 . The rings are puckered much more, so much that each niobium atom coordinates to only three tin atoms.

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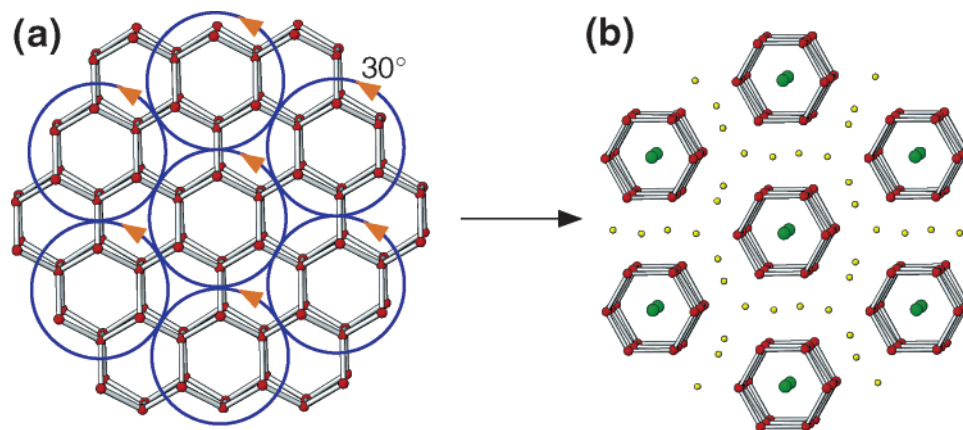


Figure 4. Structure of Na_4CaSn_6 (b) can be derived from the hexagonal diamond structure (a) by breaking bonds in the latter. This can be accomplished by a rotation of 30° of the existing tubes of stacked and interconnected cyclohexanes in the chair conformation.

The overall structure of the tin tubes in $\sigma\text{-Na}_4\text{CaSn}_6$ is very closely related to the structures of hexagonal diamond (Figure 4a) and CaIn_2 (stuffed hexagonal diamond) and can be viewed as directly derived from them. In the diamond structure each atom is four-bonded and therefore Sn^0 . Cleavage of one bond per atom and replacement of the bond with a lone pair of electrons can be accomplished by reduction with one electron per atom. This can be achieved by breaking bonds in different geometric patterns.¹⁵ The hexagonal diamond structure can be viewed as puckered layers perpendicular to the c axis that are then connected with bonds along that axis. Breaking of the latter bonds by reduction with one electron results in the CaSi_2 structure made of layers of three-bonded Si^- that are separated by Ca^{2+} .¹⁶ The hexagonal diamond can also be viewed as being made of close-packed hexagonal tubes of chairlike cyclohexanes. In this view, breaking bonds between the tubes produces the structure of Na_4CaSn_6 . This, as shown in Figure 4a, can be easily achieved by simple rotation of the tubes at 30° . This leads to exactly the same arrangement of the tubes as in Na_4CaSn_6 as shown in Figure 4b.

Another important factor for the formation of this structure is the role of the calcium cations. Generally, compared to alkali-metal cations, the alkaline-earth and divalent rare-earth cations have better capabilities to coordinate with anions because of their higher covalency and higher charge. Thus, the formation of a particular structure seems to be driven by how many such cations are present and what their preferred coordination number is. A good example for this capability is the following series of structures: NaSn ,¹⁷ $\text{Na}_{10}\text{CaSn}_{12}$,⁹ and Na_4CaSn_6 . Notice that the tin atoms in all three compounds are formally Sn^- . The first of the three can be written as $\text{Na}_{12}\text{Sn}_{12}$ and contains simple tetrahedra of Sn_4^{4-} where, of course, each tin atom is three-bonded. The second compound, as already described above, contains the truncated tetrahedra of Sn_{12}^{12-} shown in Figure 3 where, again, each tin atom is three-bonded. Finally, Na_4CaSn_6 which can be rewritten as $\text{Na}_8\text{Ca}_2\text{Sn}_{12}$ has tubes of three-bonded Sn^- . What differs in these three compounds is the number of calcium

cations. Without any Ca^{2+} in $\text{Na}_{12}\text{Sn}_{12}$, the three-bonded tin anions form the simplest and smallest possible formation with three-bonded vertexes, namely the tetrahedron. Replacing two Na^+ cations in $\text{Na}_{12}\text{Sn}_{12}$ with one Ca^{2+} results in $\text{Na}_{10}\text{CaSn}_{12}$. The preferred coordination of Ca^{2+} is apparently 12 tin atoms and this is exactly the number of atoms provided in the formula. The only possible outcome is isolated twelve-atom tin cages centered by Ca^{2+} . The cages should be as spherical as possible so that all tin atoms are equidistant from the central calcium. The only shape that satisfies these requirements is the truncated tetrahedron.

Further substitution of two Na^+ cations in $\text{Na}_{10}\text{CaSn}_{12}$ with one Ca^{2+} leads to $\text{Na}_8\text{Ca}_2\text{Sn}_{12}$ (i.e., the title compound). The ratio of tin to calcium atoms in this stoichiometry is 6:1 and, therefore, the only way to combine this ratio with the preferred coordination number of 12 for Ca^{2+} is for each tin atom to coordinate to two calcium atoms and be shared by them (i.e., $\text{CaSn}_{12/2}$). This is exactly the arrangement observed in Na_4CaSn_6 where each Ca^{2+} is coordinated by 12 tin atoms and each tin atom is coordinated to two cations in the tubes of interconnected cyclohexane-like rings.

In summary, our attempts to rationally synthesize ligand-free tin analogues of benzene failed, but a compound with the proposed stoichiometry, Na_4CaSn_6 , was synthesized and characterized. Clearly, the hypothetical Sn_6^{6-} aromatic rings are too big for coordination to calcium cations and formation of stacks that are similar to those observed for cyclopentadienyl-like Sn_5^{5-} . This large size combined with the requirement for normal Ca-Sn distances result in very short inter-ring distances and this, in turn, leads to formation of Sn-Sn bonds by puckering of the rings and loss of aromaticity. Of course, this brings the question whether larger cations may be able to stabilize the benzene-like formation. With the shortest inter-ring distance of 4.64 \AA observed for stacks of Sn_5^{5-} as a distance between hypothetical Sn_6^{6-} rings, the cation-tin distance is calculated to be 3.73 \AA . Such a distance corresponds to the largest known divalent cation, namely Ba^{2+} with an observed Ba-Sn distance of 3.70 \AA in Na_8BaSn_6 with stacks of Sn_5^{5-} .⁶ Unfortunately, the corresponding reactions designed to produce A_4BaSn_6 for $\text{A} = \text{Na}$ and K resulted in Na_8BaSn_6 and binaries, such as NaSn , KSn , and Ba_3Sn_5 .

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Supporting Information Available: X-ray crystallographic file in CIF format (3 structures), a drawing of the tin tubes in

Na₄CaSn₆ capped with sodium cations, and the magnetic susceptibilities and electrical resistivities of the three compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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