In Search of Benzene-like Sn₆⁶⁻: Synthesis of Na₄CaSn₆ with Interconnected Cyclohexane-like Sn₆⁶⁻

Iliya Todorov and Slavi C. Sevov*

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556

Received March 15, 2006

The title compound was synthesized in an attempt to produce stacked benzene-like Sn₆⁶⁻ rings separated by alkaline-earth cations in analogy with the recently reported stacks of aromatic cyclopentadienyl-like Sn₅⁻ in Na₂BaSn₆ (in addition to isolated Sn⁴⁻ 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 Sn₆⁶⁻ are puckered into chair-type cyclohexanes that are interconnected into isolated cylindrical tubes stuffed with Ca²⁺ 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 Na₁₀EuSn₁₂ and Na₁₀YbSn₁₂ which are isostructural with the known Na₁₀CaSn₁₂.

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 Al₄²⁻, Ga₄²⁻, and In₄²⁻ experimentally detected in gas phase that are both isoostructural and isoelectronic with the cyclobutadienium dication, C₄H₄²⁺.² The ones known in group 14 are the triangular Si₃²⁻ and Sn₃²⁻ in Ba₂NiSi₃ and SrSn₃, respectively; they are similarly isoostructural and isoelectronic with the cyclopropenium cation, C₃H₃⁺.³,⁴ The triangles of silicon in Ba₂NiSi₃ are stacked on top of each other in an eclipsed mode and are separated by the Ni atoms forming metallacene-like columns. The cyclopentadienyl anion, C₅H₅⁻, has also its isoostructural and isoelectronic analogues among the heavier elements of this group such as Si₅⁶⁻ in Li₃MgSi₅⁶ and the more recently characterized Sn₅⁶⁻ and Pb₅⁶⁻ in isoostructural Na₂BaSn₆ (and Na₆-EuSn₆) and Na₆BaPb₆, respectively.⁵,⁶,⁷ (Despite its analogous stoichiometry, Li₃MgSi₅⁶ 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 Ba₂NiSi₃, the rings are separated by cations in the stacks,
In Search of Benzene-like Sn$_6^{6-}$

such as lithium in Li$_2$MgSi$_6$ and alkaline-earth (or rare-earth) in the remaining compounds, and form infinite columns of metallolike-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 Li$_{9-x}$EuSn$_{6+x}$, Li$_{9-x}$CaSn$_{6+x}$, Li$_{10}$CaSn$_{11}$, and Li$_{6-}$Eu$_2$Sn$_9$ with the same columns of stacked Sn$_6^{6-}$ rings separated by the corresponding alkaline- or rare-earth cations.$^5$ 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 flat zigzag chains.$^6$\textsuperscript{7}

Finally, nearly-planar hexagonal formations of Si and Ge have been also reported: Si$_6^{10-}$ and Ge$_6^{10-}$ in Li$_2$Ba$_2$Si$_6$ and Li$_2$Ba$_2$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-$\pi^*$-orbitals, and the overall $\pi$-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 Eu and Yb analogues of Na$_4$CaSn$_6$.

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 elements (heated at 760°C for 2 weeks) and then 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 Guiner camera under vacuum, Cu K$_\alpha$, $\lambda = 1.540562$ 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 Na$_{10}$SrSn$_{12}$$^3$ and its isostructural new compounds Na$_{10}$EuSn$_{12}$ and Na$_{10}$YbSn$_{12}$, in addition to impurity-level amounts of binary phases such as NaSn, SrSn, EuSn, as well as elemental Sn. The synthesis of Na$_{10}$(RE)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$_4$CaSn$_6$, Na$_{10}$EuSn$_{12}$, and Na$_{10}$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$_\alpha$ radiation ($\lambda = 0.71073$ Å). X-ray diffraction data sets were collected at room temperature ($\omega$ = 2θ scans, $\theta_{max} = 25^\circ$). The observed extinction conditions and intensity statistics suggested the centrosymmetric space group $P6_3/mmc$ for Na$_4$CaSn$_6$ and the acincent body-centered space group $F43m$ for Na$_{10}$(RE)Sn$_{12}$ ($a = 11.2189(3)$ and 11.1768(4) Å for Na$_{10}$EuSn$_{12}$ and Na$_{10}$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.$^9$ Further details for the data collection and structure refinement of Na$_4$CaSn$_6$ are given in Table 1 (the CIF files for all three compounds are available as Supporting Information).

Properties Measurements. The magnetizations of Na$_4$CaSn$_6$, Na$_{10}$EuSn$_{12}$, and Na$_{10}$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

| Table 1. Selected Data Collection and Refinement Parameters for Na$_4$CaSn$_6$ |
|-----------------|-----------------|
| formula         | Na$_4$CaSn$_6$  |
| $fw$            | 844.18          |
| space group, $Z$| $P6_3/mmc$, 2   |
| $a$             | 10.0486(3) Å    |
| $c$             | 7.1375(3) Å     |
| $V$             | 624.15(4) Å     |
| radiation, $\lambda$ | Mo K$_\alpha$, 0.71073 Å |
| temp            | 20 °C           |
| $\rho_{\text{calc}}$ | 4.492 g cm$^{-3}$ |
| $\mu$           | 12.309 cm$^{-1}$ |
| $R1/wR2,a I \geq 2aI$ | 2.283/9.00% |
| $R1/wR2,a$ all data | 2.624/4.01% |

$^*$ $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|; wR2 = \{(\sum(w(F_o^2 - (F_c)^2))^2)/\sum(w(F_o^2))\}^{1/2}; w = |\sigma^2(F_o^2) + P(F_c)^2|/3.$

---


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 $\text{Na}_4\text{CaSn}_6$ consists of isolated tubes of tin with a repeating unit of $\text{Sn}_6^{6-}$ (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 $\text{Sn}-\text{Sn}$ 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 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 $\text{Na}_{10}\text{SrSn}_{12}$, 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 $\text{Na}_4\text{CaSn}_6$, $\text{Na}_{10}^+\text{EuSn}_{12}$, and $\text{Na}_{10}^+\text{YbSn}_{12}$, respectively. These values compare...
well with other semiconducting compounds in similar intermetallic systems such as Na₈EuSn₆ (0.09 Ω cm),⁶ Ca₁₄-Mn₆As₁₆ (0.10 Ω cm),¹¹ and Sr₁₂CdSb₁₁.₁₇ (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(ρ) versus 1/T are ca. 0.18, 0.09, and 0.21 eV for Na₄CaSn₆, Na₁₀EuSn₁₂, and Na₁₀YbSn₁₂, respectively.

Na₄CaSn₆ and Na₁₀YbSn₁₂ show temperature-independent and negative magnetic susceptibilities of \(\chi_m = C(T - \Theta)\) 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 Eu²⁺ 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 Na₈AeSn₆ compounds where Ae is an alkaline-earth (or divalent rare-earth) cation contain stacks of aromatic pentagons of Sn₆⁶⁻ and isolated Sn⁴⁺ anions, and the formula can be rationalized as (Na⁺)₈(Ae²⁺)₈(Sn₆⁶⁻)(Sn⁴⁺).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., Sn₆⁶⁻). 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 Sn₆⁶⁻ species would be Na₄AeSn₆, 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 proposed one, namely, Na₄CaSn₆. The tin substructure, however, is made of tubes of interconnected cyclohexane-like rings and not isolated benzene-like Sn₆⁶⁻. Nonetheless, this observed structure is very closely related to the proposed compound with stacked benzene-like rings, referred to as π-Na₄CaSn₆ 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 \(\sigma\)-bonded tin atoms in the observed Na₄CaSn₆, referred to as \(\sigma\)-Na₄CaSn₆.

The interplanar distance between the hypothetical benzene-like rings of eclipsed Sn₆⁶⁻ that are stacked in the hypothetical π-Na₄CaSn₆ 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 Sn₆⁶⁻ with Ca cations between them in Li₉–CaSn₆⁺, and Li₃CaSn₁₁. 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 Sn₆⁶⁻ in any of the known compounds. This difference, of course, is the result of the larger opening of the benzene-like Sn₆⁶⁻ than that of the cyclopentadienyl-like Sn₆⁶⁻ 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 \(\sigma\)-Na₄CaSn₆, 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 \(\pi–\pi\) 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 \(\pi\)-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 d⁸ square-planar platinocyanides [Pt(CN)₄]²⁻ in K₂[Pt(CN)₄]. The filled four platinum d orbitals, \(\zeta, \chi, \psi, \chi\) (analogous to the filled \(\pi\)-orbitals in Sn₆⁶⁻), 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 \(\pi\)-systems of the Sn₆⁶⁻ 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 \(\sigma\)-bonds. The \(\pi\)-system in the rings disappears by converting the low-lying \(\pi^*\)-orbitals to high-energy \(\sigma^*\)-orbitals and high-lying \(\pi\)-bonding orbitals to low-energy \(\sigma\)-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 Sn⁰). Isolated cyclohexane-like rings of Sn₆ have been characterized before as stabilized by two (tol)Nb fragments coordinated at both sides of the rings (just like calcium in Na₄CaSn₆) (i.e., [[tol]Sn₆N(tol)]²⁻).¹⁴ These species were made by a reaction of (tol)Nb with an ethylenediamine solution of the Zintl phase, K₄Sn₆. The rings are puckered much more, so much that each niobium atom coordinates to only three tin atoms.

The overall structure of the tin tubes in $\sigma$-Na$_4$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$_4$. 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. 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$^{2+}$. The hexagonal diamond can also be viewed as being made of close-packed hexagonal tubes of chair-like cyclohexanes. In this view, breaking bonds between the tubes produces the structure of Na$_4$CaSn$_6$. 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$_4$CaSn$_6$ 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, $\text{Na}_{10}$CaSn$_{12}$, and Na$_4$CaSn$_6$. Notice that the tin atoms in all three compounds are formally Sn$^-$. The first of the three can be written as Na$_1$Sn$_{12}$ and contains simple tetrahedra of Sn$_4$—where, of course, each tin atom is three-bonded. The second compound, as already described above, contains the truncated tetrahedra of Sn$_{12}$—shown in Figure 3 where, again, each tin atom is three-bonded. Finally, Na$_4$CaSn$_6$ which can be rewritten as Na$_4$CaSn$_{12}$ has tubes of three-bonded Sn$^-$. What differs in these three compounds is the number of calcium cations. Without any Ca$^{2+}$ in Na$_{10}$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 Na$_{12}$Sn$_{12}$ with one Ca$^{2+}$ results in Na$_{10}$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 Na$_{10}$CaSn$_{12}$ with one Ca$^{2+}$ leads to Na$_{12}$Ca$_2$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., Ca$_n$Sn$_{12}$). This is exactly the arrangement observed in Na$_4$CaSn$_6$ 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$_{12}$CaSn$_{12}$, was synthesized and characterized. Clearly, the hypothetical Sn$_6$ aromatic rings are too big for coordination to calcium cations and formation of stacks that are similar to those observed for cyclopentadienyl-like Sn$_6$. 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 Å observed for stacks of Sn$_6$ as a distance between hypothetical Sn$_6$-rings, the cation–tin distance is calculated to be 3.73 Å. Such a distance corresponds to the largest known divalent cation, namely Ba$^{2+}$ with an observed Ba–Sn distance of 3.70 Å in Na$_8$BaSn$_6$ with stacks of Sn$_6$. Unfortunately, the corresponding reactions designed to produce A$_2$BaSn$_6$ for A = Na and K resulted in Na$_8$BaSn$_6$ and binaries, such as NaSn, KSn, and Ba$_2$Sn$_5$.


Figure 4. Structure of Na$_4$CaSn$_6$ (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.
Acknowledgment. We thank the National Science Foundation (CHE-0446131) for the financial support of this research.

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.

IC060443P