Synthesis and Structure of the Zintl Phase SrSn$_3$Sb$_4$

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The new Zintl compound strontium tin antimonide, SrSn$_3$Sb$_4$, has been synthesized, and its structure has been determined by single-crystal X-ray diffraction methods. It crystallizes in the orthorhombic space group D_{2h}^{16}−*Pnma* with $a = 10.060(2)$ Å, $b = 4.361(1)$ Å, $c = 22.934(4)$ Å, and $Z = 4$ at 22 °C. The structure of SrSn$_3$Sb$_4$ may be described as consisting of large, narrow channels running along [010] defined by 30-membered rings constructed from an anionic framework of linked SnSb$_4$ tetrahedra, SnSb$_3$ trigonal pyramids, and zigzag Sb−Sb chains. Sr^{2+} cations are situated within these channels. The channel structures of SrSn$_3$Sb$_4$ and Ba$_2$-Sn$_3$Sb$_6$ are closely related.

Introduction

Many ternary main-group antimonides A_xM_ySb$_z$ (A = alkali metal or alkaline earth; M = triel (group 13 element) or tetrel (group 14 element)) have been discovered recently, forming a subset of an even larger class of ternary main-group pnictides $A_xM_yPn_z$ (Pn = P, As, Sb, Bi). The anionic substructures of these ternary antimonides are generally low-dimensional and show the main-group metal in tetrahedral coordination. These substructures usually comprise (i) discrete units (*e.g.*, AlSb$_4$ tetrahedra, Sb$_3$$^{7-}$ trimers, and Sb^{3-} anions in A_{14}AlSb$_{11}$ (A = Ca, Sr, Ba)),[1,2] (ii) chains (*e.g.*, corner-sharing GaSb$_4$ tetrahedra in $_∞^1$[GaSb$_3$]$^{6-}$ in Sr$_3$GaSb$_3$),[3] or (iii) layers (*e.g.*, corner-sharing MSb$_4$ tetrahedra and Sb$_2$ pairs in $_∞^2$[M_2Sb$_3$]$^{2-}$ in A_2M_2-Sb$_3$ (A = Na, K; M = Al, Ga, In)).[4–7] More rare are three-dimensional anionic substructures in which the cations may be described as residing in channels of various sizes; these occur in Na$_3$InSb$_2$ (12-membered rings)[8] and KMSb$_4$ (M = Al, Ga) (22-membered rings).[9,10] While these are not channel structures in the normal sense in which cations are easily exchangeable, such as in zeolites, it is nonetheless useful to identify this category for the purposes of classification.

In the absence of any clearer organizing scheme, the Zintl concept remains an enormously useful means of understanding the bonding in the wide variety of structures adopted in these polyanionic compounds.[11–13] (Interesting exceptions arise where the Zintl concept apparently fails, for instance, in the case of Ba$_7$Ga$_4$Sb$_9$.[14,15]) Simply put, the connectivity of the anionic framework results from the appropriate number of bonds that must form to satisfy the octet $(8 - n)$ rule, in response to the acceptance of valence electrons from the more electropositive elements in the compound. Thus, inspection of a formula such as KGaSb$_4$ immediately suggests that Sb−Sb bonding must be present in this compound.[9]

Previously we reported the synthesis of Ba$_2$Sn$_3$Sb$_6$, the first example of an ordered compound in the class of ternary alkaline earth tetrel antimonides.[16] Ba$_2$Sn$_3$Sb$_6$ forms a complex channel structure containing 30-membered rings, and we wondered whether the same structure would be adopted when Ba is substituted by another alkaline earth element, such as Sr. Given the significant difference in size of Ba^{2+} and Sr^{2+} (ionic radii of 1.42 and 1.26 Å, respectively, for CN 8),[17] the same structure would not be expected to be retained, let alone the same composition. We report here the preparation of SrSn$_3$Sb$_4$, which also possesses a channel structure. Remarkably, the anionic channel frameworks of Ba$_2$Sn$_3$Sb$_6$ and SrSn$_3$Sb$_4$ both form 30-membered rings, constructed from the *same* coordination building blocks arranged in the *same* order, but whose shape differs because of subtle changes in conformation. The relation between these structures is described, and implications on their bonding are discussed.

Experimental Section

Synthesis. SrSn$_3$Sb$_4$ was first identified as a byproduct in reactions intended to explore the effects of alkaline earth doping of various rare-earth transition-metal antimonides previously prepared in our laboratory, in the presence of a Sn flux.[18,19] The crystals used in the structure determination resulted from the reaction of a 0.25-g mixture of Sr, Hf, and Sb in a 3:1:5 ratio to which a large excess of Sn was added (Sr, 63 mg, 0.72 mmol, 99.9%, Alfa-Aesar; Hf, 43 mg, 0.24 mmol, 99.8%, Cerac; Sb, 146 mg, 1.20 mmol, 99.995%, Aldrich; Sn, 286 mg, 2.41 mmol, 99.8%, Cerac). The reactants were loaded into a quartz tube (5 cm length; 10 mm i.d.) that was then evacuated and sealed. The mixture was heated at 600 °C for 1 day and 950 °C for 2 days, cooled to 600°C over 1 day, and then cooled to room temperature over 10 h. The excess Sn was dissolved with concentrated HCl. The resulting product contained, in addition to known binary compounds, significant amounts of thin, shiny, silver, needle-shaped crystals that were found to be composed of the elements Sr, Sn, and Sb, as determined by an EDX

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Table 1. X-ray Powder Diffraction Data for $SrSn_3Sb_4^a$

hkl	d_{obs} (Å)	d_{calc} (Å)	I/I_0^b	hkl	d_{obs} (Å)	d_{calc} (Å)	I/I_0^b
103	6.114	6.093	10	216	2.499	2.498	15
104	4.998	4.987	17	402	2.457	2.458	21
112	3.781	3.780	25	316		2.184	12
113	3.546	3.547	45	020	} 2.181	2.182	77
205	3.394	3.392	81	406	2.104	2.102	10
301	3.320	3.319	42	317	2.066	2.066	10
114	3.287	3.284	10	414	2.037	2.038	70
211	3.265	3.263	100	309	2.028	2.031	17
107	3.118	3.119	12	219	2.018	2.018	60
206	3.046	3.046	22	1 1 10	1.993	1.992	13
213	3.030	3.028	37	318	1.952	1.951	20
115	3.021	3.018	89	225	1.837	1.835	27
008	2.871	2.871	60	321	1.825	1.823	14
214	2.858	2.859	17	028	1.737	1.737	26
116	2.766	2.767	76	2 0 13	1.667	1.667	11
215	2.676	2.678	11	422	1.632	1.632	12
311	2.644	2.642	95	605	1.576	1.576	17
306	2.525	2.523	14				

ᵃ The cell parameters refined from the powder pattern, obtained on a Guinier camera at room temperature, are as follows: $a = 10.064(3)$ Å, $b = 4.363(1)$ Å, $c = 22.967(6)$ Å, $V = 1008.5(4)$ Å³. *ᵇ* The intensities were calculated from the crystal structure of $SrSn_3Sb_4$ with the use of the program LAZY-PULVERIX.[22]

(energy-dispersive X-ray) analysis on a Hitachi F2700 scanning electron microscope. Anal. Calcd (mol %) for $SrSn_3Sb_4$: Sr, 12; Sn, 38; Sb, 50. Found (average of 3 analyses): Sr, 7(1); Sn, 40(2); Sb, 53(2).

Subsequently, we have attempted to synthesize $SrSn_3Sb_4$ through more rational routes, by direct stoichiometric combination of the elements at 950 °C for 2 days. The products formed are microcrystalline and consist largely of SnSb as the major phase[20] and only small amounts (~10% yield) of the ternary compound, as identified from the X-ray powder pattern obtained on an Enraf-Nonius FR552 Guinier camera (Cu Kα₁ radiation; Si standard). Better yields can be obtained in reactions containing an excess of Sr and Sb. In contrast to the synthesis of $Ba_2Sn_3Sb_6$,[16] which can be prepared in quantitative yield, $SrSn_3Sb_4$ is difficult to obtain pure. SnSb persists as an impurity in diverse reactions (including those close to the ideal composition), suggesting that $SrSn_3Sb_4$ is not necessarily a thermodynamically stable phase. The cell parameters of $SrSn_3Sb_4$ (obtained from the original reaction producing the crystals used in the structure determination) were refined from the powder diffraction data with the use of the program POLSQ.[21] Table 1 lists observed and calculated interplanar distances as well as the intensities calculated by the program LAZY-PULVERIX[22] from the single-crystal data.

Structure Determination of $SrSn_3Sb_4$. Weissenberg photography revealed Laue symmetry *mmm* and systematic extinctions (0*kl*, *k* + *l* = 2*n* + 1; *hk*0, *h* = 2*n* + 1) consistent with the orthorhombic space groups $D_{2h}^{16}-Pnma$ and $C_{2v}^9-Pn2_1a$. Final cell parameters were determined from a least-squares analysis of the setting angles of 42 reflections in the range 20° ≤ 2θ(Mo Kα) ≤ 39° centered on a Siemens P4RA diffractometer. Crystal data and further details of the data collection are given in Table 2 and the CIF file.

All calculations were carried out with the use of programs in the SHELXTL (Version 5.0) package.[23,24] Conventional atomic scattering factors and anomalous dispersion corrections were used.[25] The intensity data were processed and corrected for absorption by a semi-empirical method based on ψ-scans. The centrosymmetric space group *Pnma* was chosen on the basis of the successful structure solution and satisfactory averaging. The initial positions for all atoms were found by direct methods. Although it is not possible to distinguish between

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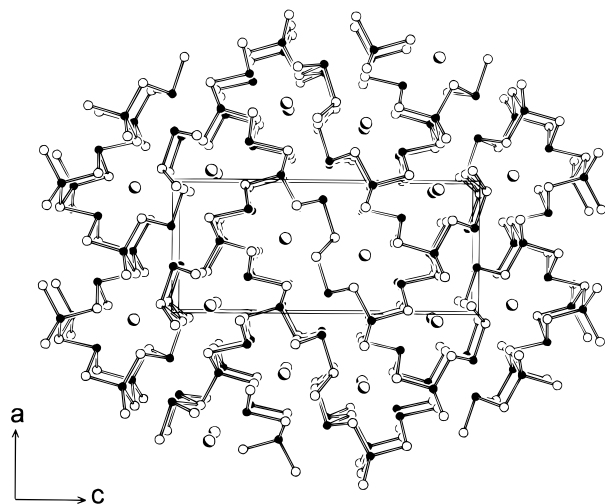(22) Yvon, K.; Jeitschko, W.; Parthé, E. *J. Appl. Crystallogr.* **1977**, *10*, 73.
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Table 2. Crystallographic Data for $SrSn_3Sb_4$

formula $SrSn_3Sb_4$	$D_{2h}^{16}-Pnma$ (No. 62)
fw 930.69	$T = 22$ °C
$a = 10.060(2)$ Å*ᵃ*	$\lambda = 0.710\,73$ Å
$b = 4.361(1)$ Å*ᵃ*	$\rho_{calc} = 6.144$ g cm⁻³
$c = 22.934(4)$ Å*ᵃ*	$\mu = 230.6$ cm⁻¹
$V = 1006.2(4)$ Å³	$R(F)$ for $F_o^2 > 2\sigma(F_o^2)^b = 0.056$
$Z = 4$	$R_w(F_o^2)^c = 0.136$

ᵃ Obtained from a refinement constrained so that α = β = γ = 90°. *ᵇ* $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. *ᶜ* $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (0.0604\,p)^2 + 0.000p]$, where $p = [\max(F_o^2,0) + 2F_c^2]/3$.

Table 3. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å²) for $SrSn_3Sb_4$

atom	Wyckoff position	x	y	z	U_{eq}^a
Sr	4c	0.0608(2)	¼	0.130 05(8)	0.0126(4)
Sn(1)	4c	0.2765(1)	¼	0.250 23(6)	0.0157(3)
Sn(2)	4c	0.3495(1)	¼	0.010 11(7)	0.0216(4)
Sn(3)	4c	0.4576(1)	¼	0.850 27(6)	0.0136(3)
Sb(1)	4c	0.0344(1)	¼	0.767 22(6)	0.0137(3)
Sb(2)	4c	0.2017(1)	¼	0.592 24(6)	0.0151(3)
Sb(3)	4c	0.2109(1)	¼	0.375 34(6)	0.0143(3)
Sb(4)	4c	0.5701(1)	¼	0.529 14(6)	0.0163(3)

ᵃ U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Sn and Sb atoms from the X-ray data alone, we postulate that an ordered model is reasonable in which the more electronegative Sb atoms are viewed as coordinating around the Sn centers. Such a model results in a chemical formula in good agreement with the elemental analysis and is consistent with the presence of tetrahedral $SnSb_4$ and trigonal pyramidal $SnSb_3$ building blocks that have been observed in related structures, such as $Ba_2Sn_3Sb_6$.[16] The structure was then refined by least-squares methods. To confirm the absence of nonstoichiometry in $SrSn_3Sb_4$, refinements were performed in which the occupancies of successive atoms were allowed to vary while the isotropic displacement parameters were fixed. These refinements resulted in occupancies of 100.2(6)% for Sr, 100.0(6)% for Sn(1), 99.0(6)% for Sn(2), 99.8(6)% for Sn(3), 100.6(6)% for Sb(1), 100.0(6)% for Sb(2), 100.4(4)% for Sb(3), and 99.6(6)% for Sb(4). The final difference electron density map is featureless ($\Delta\rho_{max} = 3.87$; $\Delta\rho_{min} = -2.93$ e Å⁻³). The atomic positions were standardized with the use of the program STRUCTURE TIDY.[26] The final cycle of least-squares refinement on F_o^2 of 50 variables (including anisotropic displacement parameters and an isotropic extinction parameter) and 1647 averaged reflections (including those having $F_o^2 < 0$) converged to residuals of $R_w(F_o^2)$ of 0.136 and $R(F)$ (for $F_o^2 > 2\sigma(F_o^2)$) of 0.056. Final values of the positional and displacement parameters are given in Table 3. Anisotropic displacement parameters are given in the CIF file, and final structure amplitudes are available from A.M.

Results and Discussion

$SrSn_3Sb_4$ adopts a new structure type, conveniently described as comprising channels that run along [010], as shown in the view down the *b* axis in Figure 1. Selected interatomic distances and angles are given in Table 4. The Sr^{2+} cations reside in the cavities within these channels. The framework of the channels is built up from $SnSb_4$ tetrahedra, $SnSb_3$ trigonal pyramids, and zigzag Sb–Sb chains. Figure 2a shows in detail how these components are connected to form one of the channels. For purposes of comparison with the structure of $Ba_2Sn_3Sb_6$ (*vide infra*), the channel may be considered to be formed from two kinds of segments. Segment *A* consists of a sequence of Sn-centered coordination polyhedra joined by corner-sharing of the Sb atoms in the following order: tetrahedron–trigonal pyramid–tetrahedron–trigonal pyramid–tetrahedron. Segment *B* consists

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Table 4. Selected Interatomic Distances (Å) and Angles (deg) for $SrSn_3Sb_4$

Sn(1)−Sb(1)	2.920(1) (2×)	Sr−Sb(2)	3.349(2) (2×)
Sn(1)−Sb(3)	2.944(2)	Sr−Sb(1)	3.350(2) (2×)
Sn(2)−Sb(2)	2.927(1) (2×)	Sr−Sb(4)	3.442(2) (2×)
Sn(2)−Sb(4)	2.952(2)	Sr−Sb(3)	3.522(2)
Sn(3)−Sb(2)	2.788(2)	Sr−Sb(4)	3.652(2)
Sn(3)−Sb(1)	2.803(2)	Sr−Sn(1)	3.508(2)
Sn(3)−Sb(3)	2.821(1) (2×)	Sr−Sn(1)	3.964(2)
Sb(4)−Sb(4)	2.920(2) (2×)	Sr−Sn(2)	4.000(2)
Sb(1)−Sn(1)−Sb(1)	96.64(5)	Sn(3)−Sb(1)−Sn(1)	92.94(5) (2×)
Sb(1)−Sn(1)−Sb(3)	90.91(5) (2×)	Sn(1)−Sb(1)−Sn(1)	96.64(6)
Sb(2)−Sn(2)−Sb(2)	96.32(6)	Sn(3)−Sb(2)−Sn(2)	98.58(4) (2×)
Sb(2)−Sn(2)−Sb(4)	91.64(5) (2×)	Sn(2)−Sb(2)−Sn(2)	96.32(6)
Sb(2)−Sn(3)−Sb(1)	102.23(6)	Sn(3)−Sb(3)−Sn(3)	101.24(6)
Sb(2)−Sn(3)−Sb(3)	115.65(4) (2×)	Sn(3)−Sb(3)−Sn(1)	86.33(5) (2×)
Sb(1)−Sn(3)−Sb(3)	111.20(5) (2×)	Sb(4)−Sb(4)−Sb(4)	96.61(9)
Sb(3)−Sn(3)−Sb(3)	101.24(6)	Sb(4)−Sb(4)−Sn(2)	108.66(6) (2×)

Figure 1. View down the *b* axis of $SrSn_3Sb_4$, with the unit cell outlined. The partly-shaded circles are Sr atoms, the solid circles are Sn atoms, and the open circles are Sb atoms.

of a similar sequence, but the middle tetrahedron is replaced by a zigzag chain of two-connected Sb(4) atoms: tetrahedron−trigonal pyramid−zigzag chain−trigonal pyramid−tetrahedron. The zigzag chains are only nominal and are identified in order to clarify the structural features; each Sb(4) atom is actually 3-bonded (to two other Sb(4) atoms and one Sn(2) atom). The tetrahedral units serve to link adjacent channels together to extend the framework along the *ac* plane (Figure 1), and corner-sharing of the coordination polyhedra along the *b* direction extends the walls of these channels to complete the three-dimensional framework.

The structure of $SrSn_3Sb_4$ bears a striking resemblance to that of $Ba_2Sn_3Sb_6$,[16] whose channel framework is depicted in Figure 2b. Remarkably, the span of these channels is identical: Both define 30-membered rings, but the one in $SrSn_3Sb_4$ is narrower while that in $Ba_2Sn_3Sb_6$ is lozenge-shaped. Both channels are built up from the same types of coordination polyhedra arranged in similar segments *A* and *B* (Figure 2). The shape of these channels depends on the orientation of the coordination polyhedra (particularly the SnSb$_4$ tetrahedra) and differences in the conformation of the smaller six-membered rings that form part of the framework. As a result, for instance, segment *A* is bent in $SrSn_3Sb_4$ but straight in $Ba_2Sn_3Sb_6$.

The alkaline earth cation clearly plays an important role in determining the shape and size of these channels. In $SrSn_3Sb_4$, the Sr^{2+} cations are bound by ionic interactions within the cavities through coordination by the surrounding Sb atoms. Figure 3 shows that the coordination can be described as roughly tricapped trigonal prismatic, if distances less than ~3.7 Å are

Figure 2. Comparison of the anionic framework of one channel in (a) $SrSn_3Sb_4$ and (b) $Ba_2Sn_3Sb_6$. Atom types are as shown in Figure 1, with the partly-shaded circles representing alkaline earth cations. The labeling of the Sn and Sb atoms in $SrSn_3Sb_4$ is indicated. The channel framework in both compounds is defined by two types of segments *A* and *B*, built up from a sequence of SnSb$_4$ tetrahedra, SnSb$_3$ trigonal prisms, and Sb−Sb zigzag chains.

accepted as the most significant. Two of each of Sb(1), Sb(2), and Sb(4) atoms at the shortest distances of 3.349(2)−3.442(2) Å form a trigonal prism. Two further Sb atoms (Sb(3) and Sb(4)) at 3.522(2)−3.652(2) Å cap faces of the trigonal prism. The third face is capped through interaction with a stereochemically active lone pair of the Sn(1) atom, at 3.508(2) Å.
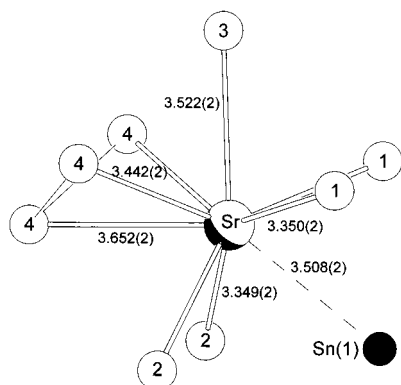
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Figure 3. Coordination of the Sr atom in SrSn$_3$Sb$_4$. Relevant interatomic distances (Å) are shown.

Distances to the next nearest atoms, at 3.964(2) and 4.000(2) Å to Sn(1) and Sn(2), respectively, are too long to be significant. In contrast, the larger Ba^{2+} cation in Ba$_2$Sn$_3$Sb$_6$ dictates a larger size for the channels, to the extent that it is further coordinated by additional Sb atoms forming isolated zigzag chains within the channel (Figure 2b).

The structure of SrSn$_3$Sb$_4$ provides another illustration of the fact that, despite the small electronegativity difference between Sn and Sb, ordered SnSb$_4$ and SnSb$_3$ units can persist. This is observed in related ternary tin antimonides, such as A_8SnSb$_4$ (A = Na, K), in which isolated tetrahedral SnSb$_4$$^{8-}$ anions occur,[27,28] or KSnSb, in which layers of corner-sharing SnSb$_3$ trigonal pyramids occur.[29-31] The Sn—Sb distances in SrSn$_3$-Sb$_4$ range from 2.920(1) to 2.952(2) Å in the SnSb$_3$ trigonal pyramids and 2.788(2)−2.821(1) Å in the SnSb$_4$ tetrahedra. These are similar to the distances found in Ba$_2$Sn$_3$Sb$_6$ (2.876-(3)−2.913(3) Å in SnSb$_3$ trigonal pyramids and 2.793(3)−2.840-(2) Å in SnSb$_4$ tetrahedra).[16] The Sb—Sn—Sb angles around the trigonal pyramidal Sn(1) and Sn(2) centers range from 90.91-(5) to 96.64(5)°, significantly smaller and indicative of greater p character compared to the angles more typical of sp^3 hybridization (101.24(6)−115.65(4)°) found around the Sn(3) atom.

Extensive Sb—Sb bonding is a recurring feature in many metal antimonides. The Sb(4)—Sb(4) distance of 2.920(2) Å corresponds to a full single bond (*cf.* 2.908 Å in elemental Sb)[32] and is comparable to those found in the isolated zigzag chains in SrSb$_2$ (2.895(2)−2.919(2) Å)[33] and Ba$_2$Sn$_3$Sb$_6$ (2.902-(3)−2.924(2) Å).[16] Channel structures in these ternary main-group antimonides are not common. The other known examples in this system are Na$_3$InSb$_2$, which contains 12-membered rings

constructed from InSb$_4$ tetrahedra only,[8] and KMSb$_4$ (M = Al, Ga), which contains 22-membered rings constructed by the condensation of alternating MSb$_4$ tetrahedra and Sb−Sb zigzag chains.[9,10] The compounds SrSn$_3$Sb$_4$ and Ba$_2$Sn$_3$Sb$_6$, whose channel structures now incorporate trigonal pyramids to form 30-membered rings, represent an extension of this series.

As noted earlier, the Sn and Sb atoms cannot be distinguished by their X-ray scattering factors alone, but as will now be demonstrated, the Zintl concept can provide a convincing argument for supporting an ordered structure. A reasonable first approximation to a bonding model can be made as follows. First, the electropositive Sr atoms are considered to transfer their valence electrons to the anionic substructure, resulting in the formulation Sr^{2+}[Sn$_3$Sb$_4$]$^{2-}$. The atoms in the anionic frame-work are either in trigonal pyramidal coordination (3-bonded) or tetrahedral coordination (4-bonded). On the basis of the (8 − n) rule and the assignment of *formal charges*, Sn^0 would be 4-bonded as found in the group 14 (IVA) elemental structures, while Sn$^-$ would be 3-bonded as found in the structures of the isoelectronic group 15 (VA) elements. Similarly, Sb^0 would be 3-bonded as found in the group 15 (VA) elemental structures, while Sb$^+$ would be 4-bonded as found in the structures of the isoelectronic group 14 (IVA) elements. The *only* distribution of formal charges consistent with both the observed crystal structure and the chemical analysis requires two of the trigonal pyramidally coordinated atoms to be Sn$^-$, and the remaining atoms to be Sn^0 (tetrahedral) and Sb^0 (trigonal pyramidal), resulting in the net charge of 2− per formula unit of [Sn$_3$Sb$_4$]. The use of formal charges is, of course, arbitrary and reflects the viewpoint that the bonds in the framework are highly covalent. The equivalent approach of using *oxidation states*, while less realistic, results in assigning tetrahedral Sn(IV) and trigonal pyramidal Sn(II), the latter exhibiting the stereochemi-cally active lone pair characteristic of that oxidation state. The structure of the related Ba$_2$Sn$_3$Sb$_6$ may be derived by inserting isolated Sb−Sb zigzag chains and charge-compensating alkaline earth cations into the structure of SrSn$_3$Sb$_4$: A^{2+} $_\infty^3$[Sn$_3$-Sb$_4$]$^{2-}$ + A^{2+} $_\infty^1$[Sb$_2$]$^{2-}$ → $(A^{2+})_2$ $_\infty^3$[Sn$_3$Sb$_4$]$^{2-}$ $_\infty^1$[Sb$_2$]$^{2-}$.

In conclusion, the synthesis of SrSn$_3$Sb$_4$, along with the previously reported Ba$_2$Sn$_3$Sb$_6$, points to the existence of a potentially rich class of Zintl compounds whose structures exploit the flexibility inherent in the combination of tetrahedra and trigonal prisms as structural building blocks. We are continuing the investigation of related systems through substitu-tion of the alkaline earth metal in the expectation of observing diverse structural variations.

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Supporting Information Available: One X-ray crystallographic file, in CIF format, is available. Access information is given on any current masthead page.

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