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Synthesis and Structure of $Ba_2Sn_3Sb_6$, a Zintl Phase Containing Channels and Chains

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The new Zintl phase dibarium tritin hexaantimonide, $Ba_2Sn_3Sb_6$ 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 $a = 13.351(1)$ Å, $b = 4.4100(5)$ Å, $c = 24.449(3)$ Å, and $Z = 4$ ($T = -50$ °C). The structure of $Ba_2Sn_3Sb_6$ comprises large channels [010] defined by 30-membered rings constructed from an anionic framework. This framework is built up from Sn-centered trigonal pyramids and tetrahedra, as well as zigzag chains of Sb atoms. Within the channels reside the Ba^{2+} cations and additional isolated zigzag Sb−Sb chains. The simultaneous presence of Sn trigonal pyramids and tetrahedra implies that $Ba_2Sn_3Sb_6$ is a mixed-valence compound whose oxidation state notation can be best represented as $(Ba^{2+})_2[(Sn^{II})_2(Sn^{IV})(Sb^{-III})_3(Sb^{-I})]^{2-}[(Sb^{-I})_2]^{2-}$.

Introduction

The Zintl concept continues to serve as a powerful unifying principle to explain the bonding in many solids classified as polar intermetallic compounds.[1−3] The compositions of these Zintl phases can be complex and their structures display a beautiful diversity of clusters, chains, nets, rings, and other polyanionic frameworks. They can be rationalized in terms of an ionic model whereby the strongly electropositive elements lose their valence electrons to the electronegative semimetals, which respond if necessary through the formation of bonds (to complete their octets) in the anionic substructure.

Numerous examples of ternary antimony-containing Zintl phases in the systems A/M/Sb, where A is an alkali metal or an alkaline earth and M is a triel (group 13) or tetrel (group 14), have been uncovered in recent years.[4−18] As part of an ongoing investigation of new low-dimensional antimonides in our laboratory, we have extended our search to such systems. While many alkali metal or alkaline earth *triel* antimonides are now known,[4,5] we were surprised to discover that there were relatively meager reports of alkali metal *tetrel* antimonides (A_8-$SnSb_4$ (A = Na, K),[6,7] A_5SnSb_3 (A = Na, K),[7,8] KSnSb,[9−11] $NaSn_2Sb_2$,[12] and Rb_4SnSb_6 [13]), and only disordered or poorly structurally characterized examples of alkaline earth *tetrel* antimonides (Mg/Si/Sb,[14,15] Mg/Sn/Sb,[16,17] and Mg/Pb/Sb[18] phase studies). We report here the synthesis and structure of $Ba_2Sn_3Sb_6$, the first example, to our knowledge, of an alkaline earth tetrel antimonide with an ordered structure. It is a Zintl phase that adopts a novel structure type presenting a delightful assortment of chains and channels in an arrangement that has not been encountered previously in related A/M/X (A = alkali metal or alkaline earth; M = triel or tetrel; X = P, As, Sb, Bi) systems. We will also demonstrate that application of the Zintl concept leads to the implication that $Ba_2Sn_3Sb_6$ is a mixed-valence compound containing tin(II) and tin(IV).

Experimental Section

Synthesis. $Ba_2Sn_3Sb_6$ was first isolated as a minor phase from the reaction of a 0.25-g mixture of BaO, La, and Sb in a 1:1:1 ratio to which a large excess of Sn was added (BaO, 93 mg, 0.60 mmol, Fisher; La, 84 mg, 0.60 mmol, 99.9%, Cerac; Sb, 74 mg, 0.60 mmol, 99.999%, Cerac; Sn, 358 mg, 3.02 mmol, 99.8%, Cerac). The reactants were loaded into a quartz tube (8-cm length, 10-mm i.d.) that was then evacuated and sealed. The mixture was heated at 600 °C for 1 day, 900 °C for 2 days, cooled to 500 °C over 1 day, and then cooled to room temperature over 5 h. After the excess Sn was dissolved with concentrated HCl, thin silver needle-shaped crystals were found in the product. Windowless EDX (energy-dispersive X-ray analysis) on a JEOL JSM-6301FXV field-emission scanning electron microscope showed that Ba, Sn, and Sb were present in these crystals, but that La and, more importantly, O were *not* present. Anal. (mol %). Calcd for $Ba_2Sn_3Sb_6$: Ba, 18; Sn, 27; Sb, 55. Found (average of four analyses): Ba, 15(2); Sn, 28(2); Sb, 57(3). The crystals obtained from this reaction, which is reproducible, were used for the single-crystal structure determination. The compound $Ba_2Sn_3Sb_6$ can also be prepared through a more rational route, by reaction of the elements in their stoichiometric proportions with the same heating profile as above. This procedure

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results in nearly phase-pure $Ba_2Sn_3Sb_6$, as revealed by the X-ray powder pattern obtained on an Enraf-Nonius FR552 Guinier camera (Cu Kα_1 radiation; Si standard). The cell parameters of this sample were refined from the powder diffraction data with the use of the program POLSQ.[19] Table 1 lists observed and calculated interplanar distances as well as the intensities calculated with the use of the program LAZY-PULVERIX[20] from the single-crystal structure.

Structure Determination of $Ba_2Sn_3Sb_6$. Preliminary cell parameters were determined from Weissenberg photographs, which revealed Laue symmetry *mmm* and systematic extinctions ($0kl$, $k + l = 2n + 1$; $hk0$, $h = 2n + 1$) 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 24 reflections in the range 20° ≤ 2θ(Mo Kα) ≤ 32° centered on an Enraf-Nonius CAD4 diffractometer. Intensity data were collected at −50 °C with the θ−2θ scan technique in the range 3° ≤ 2θ(Mo Kα) ≤ 50°. Crystal data and further details of the data collection are given in Table 2 and the Supporting Information.

Calculations were carried out with the use of the SHELXTL (Version 5.0) package.[21,22] Conventional atomic scattering factors and anomalous dispersion corrections were used.[23] Intensity data were processed, and face-indexed Gaussian-type absorption corrections were applied with the use of the program XPREP. Based on the intensity statistics, the satisfactory averaging, and the successful structure solution, the centrosymmetric space group *Pnma* was chosen. Initial atomic positions of all atoms were found by direct methods with the program XS. Given the similarity of their X-ray scattering factors, discrimination between Sn and Sb atoms is not possible. However, we believe that our proposed model is acceptable based on several observations. First, the Sn and Sb atoms are distributed among the nine crystallographically inequivalent sites (Table 3), each at a Wyckoff position 4c, such that the proportion of Sb to Sn sites agrees with that of the elemental analysis (2:1). Any other distribution results in a calculated elemental composition that is beyond that which can be accounted for by the actual chemical analysis. Second, and perhaps more convincingly, one can appeal to the chemical reasonableness of the structure, in terms of the similarity of coordination geometries and metrical details to those of

Table 1. X-ray Powder Diffraction Data for $Ba_2Sn_3Sb_6$[a]

hkl	d_{obs} (Å)	d_{calc} (Å)	I/I_o[b]	*hkl*	d_{obs} (Å)	d_{calc} (Å)	I/I_o[b]
013	3.887	3.889	10	316	2.490	2.489	17
113	3.733	3.735	32	0,0,10	2.450	2.451	11
107	3.386	3.387	46	020	2.212	2.211	82
213	3.357	3.362	10	507	2.126	2.126	10
400	3.343	3.344	14	0,0,12	2.043	2.043	12
401	3.312	3.313	41	2,1,10		2.041	32
305	3.299	3.298	54	612	1.967	1.965	36
115	3.191	3.189	84	2,1,11	1.908	1.907	13
214	3.159	3.160	32	127	1.850	1.852	16
312	3.041	3.041	62	421	1.839	1.839	15
215	2.947	2.948	53	325		1.837	20
404	2.932	2.935	11	712	1.738	1.736	10
313		2.931	82	425	1.727	1.726	20
314	2.795	2.794	47	522	1.688	1.688	11
405	2.763	2.762	39	715	1.652	1.651	11
017	2.739	2.745	19	3,1,13	1.617	1.616	15
216		2.738	100	6,1,10	1.547	1.545	10
109	2.668	2.669	12	3,0,15	1.535	1.534	10
410		2.667	12	236	1.358	1.358	13
502	2.612	2.613	20	3,2,15	1.261	1.261	12
503	2.541	2.542	10				
217		2.540	12				

[a] The cell parameters refined from the powder pattern, obtained on a Guinier camera at room temperature, are $a = 13.374(3)$ Å, $b = 4.423(1)$ Å, $c = 24.510(5)$ Å, and $V = 1449.7(4)$ Å^3. [b] The intensities were calculated from the crystal structure of $Ba_2Sn_3Sb_6$ with the use of the program LAZY-PULVERIX (Yvon, K.; Jeitschko, W.; Parthé, E. *J. Appl. Crystallogr.* **1977**, *10*, 73−74.).

Table 2. Crystallographic Data for $Ba_2Sn_3Sb_6$

formula $Ba_2Sn_3Sb_6$	D_{2h}^{16}-$Pnma$ (No. 62)
fw 1361.25	$T = -50$ °C
$a = 13.351(1)$ Å[a]	$\lambda = 0.710\ 73$ Å
$b = 4.4100(5)$ Å[a]	$\rho_{calc} = 6.281$ g cm^{-3}
$c = 24.449(3)$ Å[a]	$\mu = 214.9$ cm^{-1}
$V = 1439.5(3)$ Å^3	$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$[b] $= 0.056$
$Z = 4$	$R_w(F_o^2)$[c] $= 0.105$

[a] Obtained from a refinement constrained so that $\alpha = \beta = \gamma = 90°$. [b] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (0.0042p)^2 + 0.00p]$ where $p = [\max(F_o^2,0) + 2F_c^2]/3$.

Table 3. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for $Ba_2Sn_3Sb_6$

atom	Wyckoff position	*x*	*y*	*z*	U_{eq}[a]
Ba(1)	4c	0.1312(1)	$^1/_4$	0.10924(8)	0.0104(5)
Ba(2)	4c	0.0484(2)	$^1/_4$	0.42043(8)	0.0113(5)
Sn(1)	4c	0.0417(2)	$^1/_4$	0.24939(9)	0.0104(5)
Sn(2)	4c	0.1948(2)	$^1/_4$	0.76595(9)	0.0109(5)
Sn(3)	4c	0.3205(2)	$^1/_4$	0.40239(10)	0.0135(5)
Sb(1)	4c	0.1609(2)	$^1/_4$	0.57758(9)	0.0123(5)
Sb(2)	4c	0.3017(2)	$^1/_4$	0.00171(9)	0.0132(5)
Sb(3)	4c	0.3487(2)	$^1/_4$	0.19674(9)	0.0120(5)
Sb(4)	4c	0.3838(2)	$^1/_4$	0.81486(9)	0.0119(5)
Sb(5)	4c	0.4297(2)	$^1/_4$	0.50378(9)	0.0124(5)
Sb(6)	4c	0.5653(2)	$^1/_4$	0.64425(9)	0.0116(5)

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

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Table 4. Selected Interatomic Distances (Å) and Angles (deg) for $Ba_2Sn_3Sb_6$

Sn(1)−Sb(3)	2.894(3)	Ba(1)−Sb(2)	3.478(3)
Sn(1)−Sb(4)	2.901(2) (2×)	Ba(1)−Sb(5)	3.489(2) (2×)
Sn(2)−Sb(4)	2.793(3)	Ba(1)−Sb(6)	3.533(2) (2×)
Sn(2)−Sb(6)	2.794(3)	Ba(1)−Sb(3)	3.607(3)
Sn(2)−Sb(3)	2.840(2) (2×)	Ba(1)−Sb(1)	3.628(2) (2×)
Sn(3)−Sb(5)	2.876(3)	Ba(1)−Sb(5)	3.857(3)
Sn(3)−Sb(6)	2.913(2) (2×)	Ba(1)−Sn(1)	3.629(3)
Sb(1)−Sb(2)	2.924(2) (2×)	Ba(2)−Sb(4)	3.513(2) (2×)
Sb(5)−Sb(5)	2.902(3) (2×)	Ba(2)−Sb(1)	3.560(2) (2×)
Ba(1)−Ba(1)	4.4100(5) (2×)	Ba(2)−Sb(2)	3.580(2) (2×)
Ba(2)−Ba(2)	4.4100(5) (2×)	Ba(2)−Sb(2)	3.804(3)
		Ba(2)−Sb(3)	3.913(3)
		Ba(2)−Sn(3)	3.659(3)
Sb(3)−Sn(1)−Sb(4)	93.10(7) (2×)	Sb(2)−Sb(1)−Sb(2)	97.87(10)
Sb(4)−Sn(1)−Sb(4)	98.96(10)	Sb(1)−Sb(2)−Sb(1)	97.87(10)
Sb(3)−Sn(2)−Sb(3)	101.89(10)	Sn(2)−Sb(3)−Sn(2)	101.89(10)
Sb(4)−Sn(2)−Sb(3)	116.11(7) (2×)	Sn(2)−Sb(3)−Sn(1)	84.89(7) (2×)
Sb(6)−Sn(2)−Sb(3)	109.99(7) (2×)	Sn(2)−Sb(4)−Sn(1)	94.21(7) (2×)
Sb(4)−Sn(2)−Sb(6)	102.85(10)	Sn(1)−Sb(4)−Sn(1)	98.96(10)
Sb(5)−Sn(3)−Sb(6)	94.14(7) (2×)	Sn(3)−Sb(5)−Sb(5)	105.85(10) (2×)
Sb(6)−Sn(3)−Sb(6)	98.40(9)	Sb(5)−Sb(5)−Sb(5)	98.9(1)
		Sn(2)−Sb(6)−Sn(3)	89.08(7) (2×)
		Sn(3)−Sb(6)−Sn(3)	98.40(9)

related structures as well as its consistency with the proposed oxidation state formulation. These chemical arguments will be discussed in detail later.

Refinements were performed by least-squares methods with the program XL. Refinements in which the occupancies of successive atoms were allowed to vary (while the isotropic displacement parameters were fixed) resulted in values of 100.5(6)% for Ba(1), 100.3(6)% for Ba(2), 100.6(7)% for Sn(1), 99.9(7)% for Sn(2), 99.4(7)% for Sn(3), 99.6(7)% for Sb(1), 100.2(7)% for Sb(2), 99.4(7)% for Sb(3), 100.6(7)% for Sb(4), 99.5(7)% for Sb(5), and 99.6(7)% for Sb(6). The values of the displacement parameters are unexceptional, and the difference electron density map is featureless ($\Delta\rho_{max} = 3.24$; $\Delta\rho_{min} = -2.39$ e Å^{-3}), ruling out the possibility that interstitial oxygen atoms might be present. We thus accept the ordered, stoichiometric model $Ba_2Sn_3Sb_6$. The atomic positions were standardized with the use of the program STRUCTURE TIDY.[24] The final cycle of least-squares refinement on F_o^2 of 68 variables (including anisotropic displacement parameters and an isotropic extinction parameter) and 1443 averaged reflections (including those having $F_o^2 < 0$) converged to residuals $R_w(F_o^2)$ of 0.105 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 (Supporting Information), and final structure amplitudes are available from A.M.

Results and Discussion

Description of the Structure. A view of the structure of $Ba_2Sn_3Sb_6$ down the short *b* axis is shown in Figure 1. Selected interatomic distances and angles are given in Table 4. Gross features that can be readily discerned from this view are the large lozenge-shaped channels running along [010], zigzag Sb−Sb chains aligned within and parallel to these channels, and the isolated Ba^{2+} cations.

The large channels are defined by 30-membered rings and are constructed from an anionic framework intricately connected together by Sn and Sb atoms that display an interesting palette of coordination geometries. Figure 2 shows a more detailed view of part of this framework. The Sn atoms reside in two kinds of coordination environments. The Sn(1) and Sn(3) atoms are each bonded to three Sb atoms in a trigonal pyramidal fashion, while the Sn(2) atom is bonded to four Sb atoms in a tetrahedral fashion. The "vertical" sides of the lozenge shape of the channel (*i.e.*, parallel to the *ab* plane) are formed by sharing corners of these Sn-centered coordination polyhedra in the order tetrahedron−trigonal pyramid−tetrahedron−trigonal pyramid−tetrahedron. The other two sides (*i.e.*, parallel to the $(10\bar{1})$ or (101) planes) are formed in a similar fashion, except that an intervening zigzag Sb−Sb chain takes the place of the middle tetrahedron. The four Sn-centered tetrahedra at the corners of the lozenge serve as links to adjoining lozenges to extend the framework along the *a* direction, while the two other tetrahedra at the middle of the "vertical" sides extend the framework along the *c* direction (Figure 1). Corner-sharing of the coordination polyhedra along the *b* direction completes the three-dimensional extension of this framework. It is amusing to note the chair conformation adopted by the Sn(2)−Sb(3)−Sn(1)−Sb(4)−Sn(1)−Sb(3) atoms, and the boat conformation adopted by the Sn(1)−Sb(4)−Sn(2)−Sb(3)−Sn(2)−Sb(4) atoms (Figure 2).

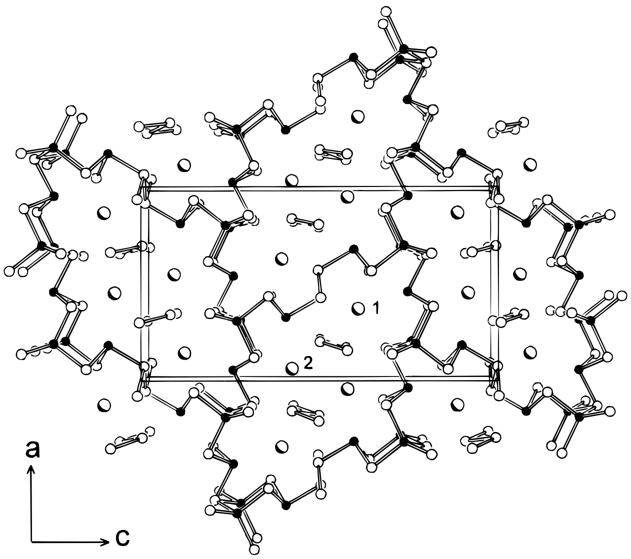

Figure 1. View down the *b* axis of $Ba_2Sn_3Sb_6$, with the unit cell outlined. The partly-shaded circles are Ba atoms, the solid circles are Sn atoms, and the open circles are Sb atoms. The two types of Ba atoms are labeled.

Within each channel reside two zigzag chains of Sb(1)−Sb(2) atoms, extending infinitely along the *b* direction. These chains are to be considered as isolated and separate from the channel framework, as the nearest distance to the framework atoms is greater than 3.6 Å.

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[24] Gelato, L. M.; Parthé, E. *J. Appl. Crystallogr.* **1987**, *20*, 139.

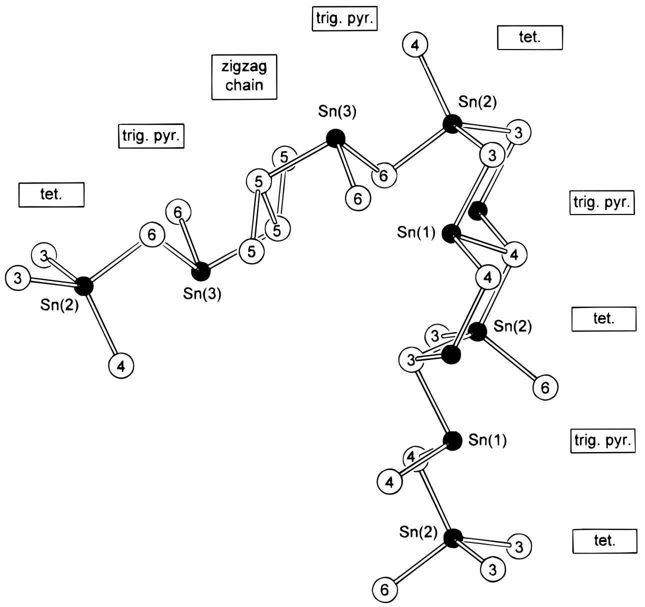

Figure 2. Detailed view of part of the anionic framework of $Ba_2Sn_3Sb_6$, showing the labeling of the Sn and Sb atoms. For clarity, only two sides making up the four-sided lozenge-shaped channels in Figure 1 are shown.

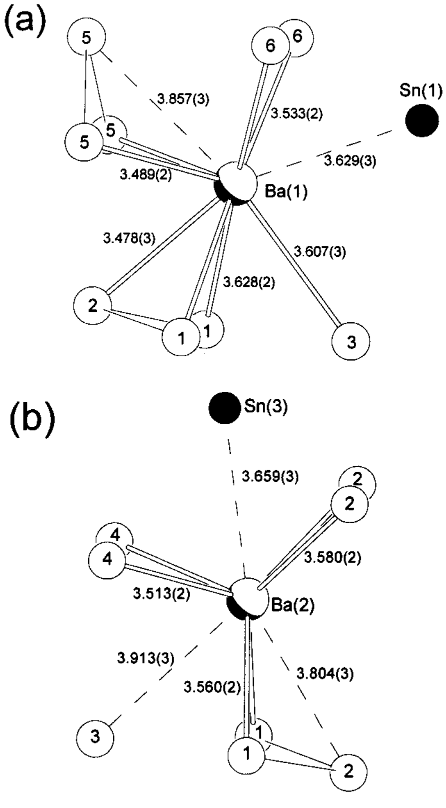

Figure 3. Coordination of the (a) Ba(1) and (b) Ba(2) atoms in $Ba_2Sn_3Sb_6$. Relevant interatomic distances (Å) are shown.

The Ba^{2+} cations are positioned within the cavities of the channel, and are coordinated by Sb atoms of the anionic framework as well as those of the isolated zigzag chains. The Ba(1) atom is coordinated in a highly irregular fashion by eight Sb atoms at distances of 3.478(3)–3.628(2) Å, as shown in Figure 3a. The distance of 3.857(3) Å to a ninth Sb atom is probably too long to be important. However, the Ba(1)–Sn(1) distance of 3.629(3) Å cannot be ignored, and indeed lies along a direction that would seem to indicate an interaction to a stereochemically active lone pair on Sn(1). The coordination around the Ba(2) atom is a little more regular, with distances of 3.513(2)–3.580(2) Å to six Sb atoms in a trigonal prismatic environment, as shown in Figure 3b. The next nearest Ba(2)–Sb distances of 3.804(3) and 3.913(3) Å are probably unimportant. Again, the Ba(2)–Sn(3) distance of 3.659(3) Å may bear some significance.

Structural Relationships and Bonding. In its overall form, $Ba_2Sn_3Sb_6$ resembles the structure of $KMSb_4$ (M = Al, Ga) in that they also possess channels defined by smaller 22-membered rings formed by MSb_4 tetrahedra.[40,p] Fragments of the $Ba_2Sn_3Sb_6$ structure are reminiscent of features found in related antimonides. The tetrahedral $Sn(2)Sb_4$ unit in $Ba_2Sn_3Sb_6$ has Sn–Sb distances of 2.793(3)–2.840(2) Å; these distances are comparable to those found in the isolated tetrahedra in Na_8SnSb_4 (2.843(1) Å)[6] and K_8SnSb_4 (2.898(1) Å),[7] the edge-sharing tetrahedral dimers in K_5SnSb_3 (2.818(1)–2.886(1) Å),[8] and the infinite corner-sharing tetrahedral chains in Na_5SnSb_3 (2.805(1)–2.945(1) Å).[7] The Sb–Sn(2)–Sb angles in the $Sn(2)Sb_4$ tetrahedron range from 101.89(10) to 116.11(7)°, slightly distorted from the ideal tetrahedral angle. The trigonal pyramidal $Sn(1)Sb_3$ and $Sn(3)Sb_3$ units in $Ba_2Sn_3Sb_6$ have Sn–Sb distances of 2.894(3)–2.901(2) and 2.876(3)–2.913(2) Å, respectively. These are similar to the 2.883(2) Å distances found in the $SnSb_3$ trigonal pyramids in KSnSb.[9] The Sb–Sn(1)–Sb and Sb–Sn(3)–Sb angles are considerably reduced (93.10(7)–98.96(10) and 94.14(7)–98.40(9)°, respectively) from the ideal tetrahedral angles, consistent with the greater *p* character of the Sn–Sb bonds in such units. All of these Sn–Sb distances are close to 2.81 Å, the sum of the Pauling covalent radii of Sn and Sb atoms.[25]

Two kinds of zigzag Sb–Sb chains are present in the structure of $Ba_2Sn_3Sb_6$. One kind forms part of the channel framework and has Sb(5)–Sb(5) distances of 2.902(3) Å and angles of 98.9(1)°. The other is isolated on its own and has Sb(1)–Sb(2) distances of 2.924(2) Å and angles of 97.87(10)°. Isolated zigzag Sb–Sb chains also occur, for instance, as the anionic part of the Zintl phases $CaSb_2$ and $SrSb_2$; these chains have Sb–Sb distances of 2.915(1)–2.939(1) and 2.895(2)–2.919(2) Å, respectively.[26,27] These values are close to the 2.908 Å distance found in elemental antimony.[28]

We are now in a position to propose a bonding model for $Ba_2Sn_3Sb_6$. Applying the Zintl concept results in the partial formulation $(Ba^{2+})_2[Sn_3Sb_6]^{4-}$. If we assume that full two-electron single Sb–Sb bonds occur in the isolated zigzag chains, the oxidation states $Sb(1)^{-I}$ and $Sb(2)^{-I}$ can be assigned for these two-bonded Sb atoms. The three-coordinate Sb atoms forming part of the channel framework are assigned all of the electrons in their octets, being the more electronegative partners of the Sn–Sb bonds, resulting in $Sb(3)^{-III}$, $Sb(4)^{-III}$, and $Sb(6)^{-III}$. The Sb(5) atom also forms two single Sb–Sb bonds to symmetry equivalents of itself, and are assigned as $Sb(5)^{-I}$. The assignment of Sb^{-I} in the zigzag chains is consistent with that of $Sr^{II}(Sb^{-I})_2$,[27] for instance. Proceeding to the Sn atoms, we conclude that those in the trigonal pyramidal coordination must be $Sn(1)^{II}$ and $Sn(3)^{II}$, while that in the tetrahedral coordination must be $Sn(2)^{IV}$. Again, this is consistent with the assignment of trigonal pyramidal[9] Sn^{II} in $K^{I}Sn^{II}Sb^{-III}$ and tetrahedral Sn^{IV} in $(K^{I})_8(Sn^{IV})(Sb^{-III})_4$ or $(Na^{I})_5(Sn^{IV})(Sb^{-III})_3$.[7] Note also the slightly longer Sn–Sb distances in the trigonal pyramids (Table 4), in agreement with the larger size expected

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(25) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.
(26) Deller, K.; Eisenmann, B. *Z. Anorg. Allg. Chem.* **1976**, *425*, 104.
(27) Deller, K.; Eisenmann, B. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1976**, *31*, 1146.
(28) Donohue, J. *The Structures of the Elements*; Wiley: New York, 1974.

for Sn^{II}. The presence of a stereochemically active lone pair on the Sn^{II} atoms is evident, given that it points inside the channel in an orientation that allows it to interact with the Ba^{2+} cations. Thus, $Ba_2Sn_3Sb_6$ is also interesting in being a *mixed-valence* compound. It is convenient to give the crystal chemical formulation as: $(Ba^{2+})_2\,{}^{3}_{\infty}[(Sn^{II})_2(Sn^{IV})(Sb^{-III})_3(Sb^{-I})]^{2-}\,{}^{1}_{\infty}[(Sb^{-I})_2]^{2-}$, in which the separate anionic substructures of the channel framework and the isolated zigzag chains are explicitly indicated.

The bonding model above was based on the assignment of *oxidation states*, a useful notion that helps to rationalize the coordination geometries of the Sn atoms in the structure. However, given the similar electronegativities of Sn and Sb, it should not be thought that the actual charge distribution resembles as extreme a situation as implied by the oxidation state assignment, which is, after all, a formalism. Rather, the Sn−Sb bonds are expected to be highly covalent. The alternative but equivalent approach based on *formal charges* leads to the assignment of 3-bonded Sn^{1-}, 4-bonded Sn^{0}, 2-bonded Sb^{1-}, and 3-bonded Sb^{0}. When different isosteric combinations are considered for the anionic substructure,[1] the same conclusion is reached for the distribution of Sn and Sb atoms as before.

In conclusion, the preceeding arguments strongly support an ordered, stoichiometric model for the structure of the novel compound $Ba_2Sn_3Sb_6$, which provides a good example of the structural diversity that Zintl phases can adopt. The anionic framework is remarkable for its combination of heteroatomic associations (Sn−Sb) with homoatomic ones (Sb−Sb). It will be interesting to see if the same structure is retained upon substitution of the alkaline earth. Mössbauer spectroscopy would be helpful in confirming the mixed-valent nature of the Sn atoms, as the chemical isomer shifts of trigonal pyramidal and tetrahedral Sn atoms should be resolvable.[12] We envisage measuring the physical properties and attempting to formulate a more quantitative description of the bonding through electronic band structure calculations.

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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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