

Solid State Compounds with Tin–Tin Bonding. $\text{Yb}_{36}\text{Sn}_{23}$: A Novel Compound Containing Oligomeric Tin Anions

E. Alejandro Leon-Escamilla and John D. Corbett*

Department of Chemistry and Ames Laboratory—DOE,¹ Iowa State University, Ames, Iowa 50011

Received July 22, 1998

Reaction of appropriate amounts of the elements in Ta at 1100 °C leads to formation of the title phase in high yield. Hydrogen impurities in small amounts do not obscure its formation. $\text{Yb}_{36}\text{Sn}_{23}$ crystallizes in tetragonal space group $P4/mbm$ (No. 127) with $a = 12.3869(5)$ Å, $c = 22.935(1)$ Å, $Z = 2$. The structure features a linear tin hexamer, five dimers, and seven isolated tin atoms per formula unit. These proportions lead to a closed-shell oxidation state count for simple octet assignments $(\text{Yb}^{+2})_{36}(\text{Sn}_6^{-14})(\text{Sn}_2^{-6})_5(\text{Sn}^{-4})_7$ and a Zintl phase classification. Dimensionally, all cations appear to be Yb^{II} . The hexamer of tin atoms has as its genesis the close contact of Sn atoms that center confacial square antiprismatic arrangements of Yb atoms (closely related to the parent W_5Si_3 structure). These interconnect with elongated square prisms in a 6:1 proportion to generate the $n = \text{six}$ member of Parthé's homologous series $\text{A}_{5n+6}\text{B}_{3n+5}$. Electrical conductivity measurements as a function of temperature show that the compound is a poor metal ($\rho_{298} \approx 130 \mu\Omega\cdot\text{cm}$). The latter property is not uncommon for compounds containing clusters of the early p elements.

Introduction

Exploration of the *anionic* chemistry of the post-transition main-group (p) elements has been delightful and rewarding in the variety of novel clusters and networks that can be found in their compounds with the active metals.² The great majority of these are also valence compounds (Zintl phases) in modern bonding terms, or close to this limit. Among these systems, the tendency of tin to form classical octet-rule homoatomic polyanions has been particularly remarkable. These have included condensed pentagonal-faced dodecahedra in K_8Sn_{25} , a defect clathrate-I structure in K_8Sn_{44} , etc.,³ a tunnel structure in NaGaSn_2 ⁴ in which the anionic network is isoelectronic with gray tin, a complex 3D network in $\text{Na}_5\text{Sn}_{13}$,⁵ an intergrowth structure containing dimeric and linear pentameric tin oligomers in $\text{Ca}_{31}\text{Sn}_{20}$,⁶ and zigzag chains built of interconnected square planar (and in this case, hyperelectronic) Sn_5^{-14} units in $\text{Ca}_{6.2}\text{Mg}_{3.8}\text{Sn}_7$.⁷

The discovery of another example, the novel binary phase $\text{Yb}_{36}\text{Sn}_{23}$, resulted from our continuing interest in the effects of hydrogen on the family of 5:3 compounds comprising the alkaline-earth (Ae = Ca, Sr, or Ba) and divalent rare-earth-metal (R = Sm, Eu, Yb) pnictides (Pn = As, Sb, Bi) and tetrelides (Tt = Si, Ge, Sn, Pb).⁸ We have in the course of this demonstrated that adventitious hydrogen can generate numerous very stable ternary $(\text{Ae,R})_5(\text{Pn,Tt})_3\text{H}$ compounds and thereby

obscure the existence of truly binary phases. For instance, the discovery of several members of the $(\text{Ae,R})_{16}\text{Pn}_{11}$ ($\text{Ca}_{16}\text{Sb}_{11}$ -type) family⁹ as well as the existence of certain Mn_5Si_3 -type examples had been precluded by the presence of very stable hydrides with the orthorhombic $\text{Ca}_5\text{Sb}_3\text{F}$ (formerly $\beta\text{-Yb}_5\text{Sb}_3$)-type structure.¹⁰ Comparable effects have also been demonstrated in tetrelide systems, such that several reported Ae_5Tt_3 phases with Cr_5B_3 -type structures are actually ternary hydrides (stuffed Cr_5B_3 - or $\text{La}_5\text{Pb}_3\text{O}$ -type).^{8,11}

It was our examination of the specific Yb–Sn system around the composition Yb_5Sn_3 that led to the discovery of $\text{Yb}_{36}\text{Sn}_{23}$. A previous report of both Mn_5Si_3 - and Cr_5B_3 -type phases at this composition¹² originated with impurities and could not be reproduced in the clean binary system. We describe here the synthetic studies, a single-crystal X-ray structure determination, and some electrical and magnetic property measurements on the new $\text{Yb}_{36}\text{Sn}_{23}$ with its novel mixture of monomeric, dimeric, and hexameric tin anions. These yield a formulation that is consistent with Zintl phase concepts.² The compound is also the first $n = \text{six}$ member of structural series $\text{A}_{5n+6}\text{B}_{3n+5}$ ¹³ originating from W_5Si_3 -type slabs.¹⁴ We have earlier reported on the $n = 2$ and 5 members of this series, $\text{Ca}_{16}\text{Sb}_{11}$ ⁹ and $\text{Ca}_{31}\text{Sn}_{20}$ ($\text{Pu}_{31}\text{Pt}_{20}$ -type¹⁵), respectively.

Experimental Section

Synthesis. All materials were handled in low-humidity gloveboxes (<0.1 ppm H_2O) filled with He or N_2 and following standard techniques.^{6,9,10} The elements were loaded into Ta tubes that were

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Table 1. Selected Crystallographic Data and Refinement Parameters for Yb₃₆Sn₂₃

fw	8959.31
space group, Z	<i>P4/mbm</i> (No. 127), 2
lattice params ^a	
<i>a</i> (Å)	12.3869(5)
<i>c</i> (Å)	22.935(1)
vol (Å ³)	3519.0(3)
density, calcd (g/cm ³)	8.455
abs. coeff (cm ⁻¹ , Mo Kα)	551.9
<i>R/R_w</i> ^b (%)	3.1/3.6

^a Lattice parameters calculated from Guinier powder pattern data, $\lambda = 1.540\ 562\ \text{Å}$, 23 °C. ^b $R = \sum |F_o| - |F_c| / \sum |F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$; $w = \sigma_F^{-2}$.

subsequently arc-welded shut under Ar and jacketed in fused silica containers. The silica containers were in these cases connected to a high-vacuum line in order to run high-temperature reactions under continuous vacuum to ensure the absence of hydrogen, Ta being permeable to hydrogen above about 550 °C.¹⁶ Products containing Yb₃₆Sn₂₃ in high yield (>90%, as subsequently estimated on the basis of a calculated Guinier powder pattern) were obtained on reaction of the appropriate mixture of Yb (99.99%, Ames Lab.) and Sn (99.999%, Aesar). Higher yields of the title phase were obtained for compositions slightly richer in Yb, i.e., 5Yb + 3Sn (62.5 rather than the theoretical 61.0 atom % Yb), probably because of Yb metal losses through volatility. The reactants were generally held under vacuum at 1150 °C for 2–4 h and then slowly cooled (10 °C/h) to 650 °C. Conversely, only slightly lower yields of the title phase were obtained when the high-quality Yb metal was used as provided and the silica jackets were sealed off before heating. In this case, dehydration of the silica contributes a hydrogen source as well.¹⁷ These low hydrogen concentrations did not appear to interfere with the formation of Yb₃₆Sn₂₃; however, small amounts of impurity phases (<3–5%) might have been missed in the relatively complex powder pattern of the target phase. On the other hand, reactions loaded with excess hydrogen, viz., Yb₅Sn₃H₄ (2YbH₂ + 3Yb + 3Sn), yielded 10–15% of a Yb₅Sn₃H_x phase with the stuffed Cr₅B₃-type structure.⁸

Powder X-ray Diffraction. Powder patterns were obtained from small ground samples held between cellophane tape. An Enraf-Nonius Guinier camera, Cu Kα1 radiation ($\lambda = 1.540\ 56\ \text{Å}$), and Si (NIST) as an internal standard were employed. The Guinier patterns were digitized with an LS20 line scanner (KEJ Instruments, Stockholm, Sweden) and standardized according to the Si line positions with the program SCANPI8.¹⁸ Lattice parameters of the sample were then calculated by least-squares of indexed 2θ data. There is considerable resemblance of the experimental pattern of Yb₃₆Sn₂₃ to those of related Pt₃₁Pu₂₀-type phases Ca₃₁Sn₂₀, Sr₃₁Pb₂₀, and Yb₃₁Pb₂₀, appropriate to their structural similarities.

Single-Crystal Structure Study. A black platelike crystal 0.23 × 0.18 × 0.10 mm was mounted in a glass capillary inside the glovebox and checked for singularity through Laue photographs. One quadrant of diffraction data ($2\theta_{\max} = 50^\circ$) was collected at room temperature on an Enraf-Nonius CAD4 automatic diffractometer with Mo Kα radiation according to the tetragonal cell determined from indexing of 25 centered reflections. Some details of the data collection and refinement are listed in Table 1. The diffraction data were corrected for Lorentz polarization effects and for adsorption empirically with the aid of three ψ -scans. Later, a more thorough absorption correction ($\mu = 551.9\ \text{cm}^{-1}$) by DIFABS¹⁹ was applied before anisotropic refinement, and this yielded generally smaller thermal ellipsoids.

On the basis of the systematic absences, the space groups *P4bm* (No. 100), *P4b2* (117), and *P4/mbm* (127) were possible. Only the last space group provided a model with good statistics from a direct methods approach (SHELX86),²⁰ and this contained the correct positions of all

Table 2. Refined Positional Parameters of and Isotropic-Equivalent Ellipsoids for Yb₃₆Sn₂₃

atom	Wyckoff position			<i>B_{eq}</i> (Å ²) ^a
	x	y	z	
Sn1	2 <i>a</i>	0	0	1.0(1)
Sn2	4 <i>e</i>	0	0	0.1663(1)
Sn3	4 <i>e</i>	0	0	0.3018(1)
Sn4	4 <i>e</i>	0	0	0.4336(1)
Sn5	4 <i>g</i>	0.0884(2)	$x + 1/2$	0
Sn6	4 <i>h</i>	0.1569(2)	$x + 1/2$	$1/2$
Sn7	8 <i>k</i>	0.1641(1)	$x + 1/2$	0.2156(1)
Sn8	8 <i>k</i>	0.3059(1)	$x + 1/2$	0.1308(1)
Sn9	8 <i>k</i>	0.3484(1)	$x + 1/2$	0.3595(1)
Yb1	4 <i>f</i>	0	$1/2$	0.12807(9)
Yb2	4 <i>f</i>	0	$1/2$	0.2789(1)
Yb3	4 <i>f</i>	0	$1/2$	0.4293(1)
Yb4	4 <i>g</i>	0.3330(1)	$x + 1/2$	0
Yb5	8 <i>j</i>	0.0824(1)	0.2199(1)	$1/2$
Yb6	16 <i>l</i>	0.41239(8)	0.28485(9)	0.36815(5)
Yb7	16 <i>l</i>	0.07601(8)	0.21237(9)	0.23792(4)
Yb8	16 <i>l</i>	0.05618(8)	0.79001(9)	0.09202(4)

$$^a B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^*$$

atoms. The structure subsequently was refined with the aid of the TEXSAN package.²¹ The final cycle of full-matrix least-squares refinement with 1205 observed reflections ($I > 3\sigma_I$) and 88 variables (all positional and anisotropic thermal parameters) converged at $R(F)/R_w = 0.031/0.036$. No significant deviation from full atom occupancies was evident. Table 2 gives the atomic positional and isotropic-equivalent thermal parameters, and Table 3 lists important interatomic distances in the structure. More crystallographic and refinement data as well as the anisotropic displacement parameters are contained in the Supporting Information, and the F_o/F_c listing along with the other information is available from J.D.C.

Properties. Electrical resistivity data were measured at 35 MHz over 150–300 K by the electrodeless “Q” method²² with the aid of a Hewlett-Packard 4342A Q Meter. For this purpose, approximately 100 mg of powdered sample with an average grain diameter of 500 μm was dispersed with nearly eight times as much chromatographic Al₂O₃ and sealed under He in a Pyrex tube. Magnetic susceptibility measurements were made on two different preparations. These were held between two silica rods within a close-fitting silica tube and were measured under He at 3 T over the range 6–300 K on a Quantum Design MPMS SQUID magnetometer. The raw data were corrected for susceptibilities of the container and the ion cores.

Results and Discussion

Syntheses. The most recent Yb–Sn phase diagram report by Palenzola and Cirafici¹² indicates that both hexagonal Mn₅Si₃-type and tetragonal Cr₅B₃-type phases exist near 62.5 atom % Yb, the latter being observed above 1090 °C. Neighboring phases are Yb₅Sn₄ (55.5 atom % Yb) and Yb₂Sn (66.7 atom % Yb) with the Gd₅Si₄ and Ni₂In structure types, respectively. Our findings in this system (see Experimental Section) are that Yb₃₆Sn₂₃ (61.0 atom % Yb) forms in high yield on cooling samples in the composition range 60.8–62.5 atom % Yb from 1150 °C. Hydrogen in low concentrations, either purposely loaded as YbH₂ or as an inadvertent impurity, does not obscure the formation of Yb₃₆Sn₂₃. This was demonstrated by parallel reactions carried out under dynamic vacuum (to remove hydrogen) or in sealed containers in the presence of low concentrations of hydrogen. On the other hand, reactions with excess hydrogen lead to a ternary Yb₅Sn₃H product with a stuffed Cr₅B₃-type

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Table 3. Interatomic Distances (<4.5 Å) in Yb₃₆Sn₂₃

atom-atom		<i>d</i> (Å)	atom-atom		<i>d</i> (Å)
Sn1-Sn2	(×2)	3.814(3)	Yb3-Sn6	(×2)	3.190(3)
Yb8	(×8)	3.421(1)	Sn9	(×2)	3.100(3)
Sn2-Sn3		3.107(5)	Yb2		3.451(2)
Yb7	(×4)	3.241(2)	Yb3		3.242(4)
Yb8	(×4)	3.186(2)	Yb5	(×4)	3.963(2)
Sn3-Sn2		3.107(5)	Yb6	(×4)	3.949(1)
Sn4		3.023(5)	Yb4-Sn5	(×2)	3.310(3)
Yb6	(×4)	3.256(2)	Sn5		4.285(4)
Yb7	(×4)	3.154(2)	Sn8	(×2)	3.037(2)
Sn4-Sn3		3.023(5)	Yb8	(×4)	3.797(1)
Sn4		3.046(7)	Yb8	(×4)	4.062(2)
Yb5	(×4)	3.283(2)	Yb5-Sn4	(×2)	3.283(2)
Yb6	(×4)	3.245(2)	Sn6		3.323(4)
Sn5-Sn5		3.098(7)	Sn6		3.334(2)
Yb1	(×2)	3.321(2)	Sn9	(×2)	3.695(2)
Yb4	(×2)	3.310(3)	Yb3		3.963(2)
Yb4		4.285(4)	Yb5		3.464(3)
Yb8	(×4)	3.294(2)	Yb6	(×2)	3.685(1)
Sn6-Yb3	(×2)	3.190(3)	Yb6	(×2)	3.812(1)
Yb5	(×2)	3.323(4)	Yb6-Sn3		3.256(2)
Yb5	(×2)	3.334(2)	Sn4		3.245(2)
Yb6	(×4)	3.520(1)	Sn6		3.520(1)
Sn7-Sn8		3.156(3)	Sn7		3.921(2)
Yb1		3.506(3)	Sn9		3.331(2)
Yb2		3.219(3)	Sn9		3.397(1)
Yb6	(×2)	3.921(2)	Yb3		3.949(1)
Yb7	(×2)	3.315(2)	Yb5		3.685(1)
Yb7	(×2)	3.384(1)	Yb5		3.812(1)
Yb8	(×2)	3.501(2)	Yb6		3.455(2)
Sn8-Sn7		3.156(3)	Yb6	(×2)	4.070(2)
Yb1		3.401(2)	Yb7		3.610(1)
Yb4		3.037(2)	Yb7		3.779(1)
Yb7	(×2)	3.086(2)	Yb7-Sn2		3.241(2)
Yb8	(×2)	3.224(2)	Sn3		3.154(2)
Yb8	(×2)	3.437(2)	Sn7		3.315(2)
Sn9-Yb2		3.236(3)	Sn7		3.384(1)
Yb3		3.100(3)	Sn8		3.086(2)
Yb5	(×2)	3.695(2)	Sn9		3.391(2)
Yb6	(×2)	3.331(2)	Yb2		3.803(1)
Yb6	(×2)	3.397(1)	Yb6		3.610(1)
Yb7	(×2)	3.391(2)	Yb6		3.779(1)
Yb1-Sn5	(×2)	3.321(2)	Yb7		3.707(2)
Sn7	(×2)	3.506(3)	Yb7	(×2)	3.951(2)
Sn8	(×2)	3.401(2)	Yb8		3.726(1)
Yb2		3.459(3)	Yb8-Sn1		3.421(1)
Yb8	(×4)	3.751(1)	Sn2		3.186(2)
Yb2-Sn7	(×2)	3.219(3)	Sn5		3.294(2)
Sn9	(×2)	3.236(3)	Sn7		3.501(2)
Yb1		3.459(3)	Sn8		3.224(2)
Yb3		3.451(2)	Sn8		3.437(2)
Yb7	(×4)	3.803(1)	Yb1		3.751(1)
			Yb4		3.797(1)
			Yb4		4.062(2)
			Yb7		3.610(1)
			Yb8	(×2)	3.808(2)

structure, a phase previously misidentified as Yb₅Sn₃. We also believe that their Yb₅Sn₄ is a hydride.⁸ Because of the large amount of data, our studies on the effects of hydrogen on the alkaline-earth and divalent rare-earth-metal tetrelides and details on these so-called A₅Tt₃ "binaries" will be the subject of a later manuscript.¹¹ The earlier observation of a Mn₅Si₃-type structure as well in the binary system¹² must have originated from a Yb₅Sn₃Z phase because of substantial impurities, Z = C, N, O,²³ We have been unable to obtain such a structure type in either of the Yb₅Sn₃ or Yb₅Sn₃H systems, although they do occur for Sm and Yb tetrel hydride systems.

Structure of Yb₃₆Sn₂₃. This novel phase crystallizes in a primitive tetragonal cell, *P4/mbm*, with 17 independent atom

positions, nine Sn and eight Yb, and exhibits as its main features a remarkable linear tin hexamer, five tin dimers, and seven isolated tin atoms dispersed among Yb atoms in the independent unit (*Z* = 2). Figures 1 and 2 are [001] and [100] views of the cell, respectively, with tin drawn as smaller solid spheres. The heavy lines between the Sn atoms denote short contacts, presumably bonds. The Yb₃₆Sn₂₃ structure can be considered the *n* = six member of Parthé's homologous series, A_{5*n*+6}B_{3*n*+5}.¹³ This series exhibits an infinite array of B atoms (Sn here) that center confacial antiprisms and square prisms of A (Yb) atoms that are joined along the *z* direction in a 6:1 sequence. Each square antiprism forms part of a slab that can be related to the W₅Si₃-type parent structure (*n* = ∞). Large distortions of the parent structure are observed closer to where the single slab containing square prismatic A_{8/2}B units is intergrown with the others. (The W₅Si₃-type structure consists of two polyhedral fragments, square antiprisms built of W1 and centered by Si that form confacial chains along 0,0,*z* and 1/2,1/2,*z*, and parallel chains of tetrahedral [(Si₂)₄W2] units that share Si edges along 0,1/2,*z*, etc. The latter silicon atoms also bridge shared antiprism edges on two chains of the first type (see Figure 3a). Nearly all compounds that crystallize in the W₅Si₃ structure show short M-M contacts between the atoms in the W2 position (0,1/2,1/4).)

Reminiscent of Ca₃₁Sn₂₀ (*n* = 5),⁶ which contains a linear pentamer in a related structure, the independent half of the Yb₃₆Sn₂₃ structure can be described in terms of four slab sections centered at *z* ≈ 0.43, 0.30, 0.17, and 0. The first section at *z* ≈ 0.43 depicted in Figure 3a is essentially that of W₅Si₃, and it is mirrored by an identical slab centered at *z* ≈ 0.57. This contains square antiprisms built of Yb5 and Yb6 atoms that are centered by Sn4 atoms at 0,0,0.43 and 1/2,1/2,0.43 and interconnected by isolated edge-bridging Sn6 and Sn9 atoms bonded to adjacent square antiprisms. (Sn4 is one of the central pair in the Sn₆ unit along this channel, as can be followed with the aid of Figure 4a.) The Sn6 and Sn9 atoms are also members of the edge-sharing tetrahedra that surround the Yb3 atoms along 0,1/2,*z*. The second section at *z* ≈ 0.30 (not depicted) is nearly equivalent to the first, but the squares of Yb6 and Yb7 atoms constituting the antiprisms have twisted a little and are now centered by Sn3 in the hexamer. The third section at *z* ≈ 0.17, Figure 3b, shows the related network around the Sn2 atoms that lie at the ends of the hexamer. Here, the squares of Yb7 and Yb8 have twisted anew, and Sn7 and Sn8 that bridge their edges have now formed dimers by opening the shared edges of the nominal tetrahedra. This section is still related to the W₅Si₃-type structure. In the fourth section at 0,0,0, Figure 3c, there are now Yb8 square prisms centered by Sn1 plus in-plane Sn5 dimers, formerly one edge of the tetrahedra along 0,1/2,*z*, that have displaced into cavities at 0,1/2,0. At this point, the principal features of the W₅Si₃-type structure have been lost. The oversized square prismatic arrangement is probably the origin of the somewhat larger but fairly spherical thermal ellipsoids found for the Sn1 atom (Table 2). Similar peculiarities were observed for Sn1 in Ca₃₁Sn₂₀,⁶ and a more extreme situation was found in a square prismatic cavity in Ca₁₆Sb₁₁,⁹ where disorder of the centering atom was discerned. Despite the distortions in this structure, all self-bonded Sn atoms remain eight-coordinate by Yb, following the general construction motif of the layers, while the isolated Sn6 and Sn9 have 10 Yb neighbors.

The confacial chains of six antiprismatic polyhedra of Yb atoms centered by Sn, with a perpendicular mirror plane at the center, is the origin of the linear hexamer in the structure.

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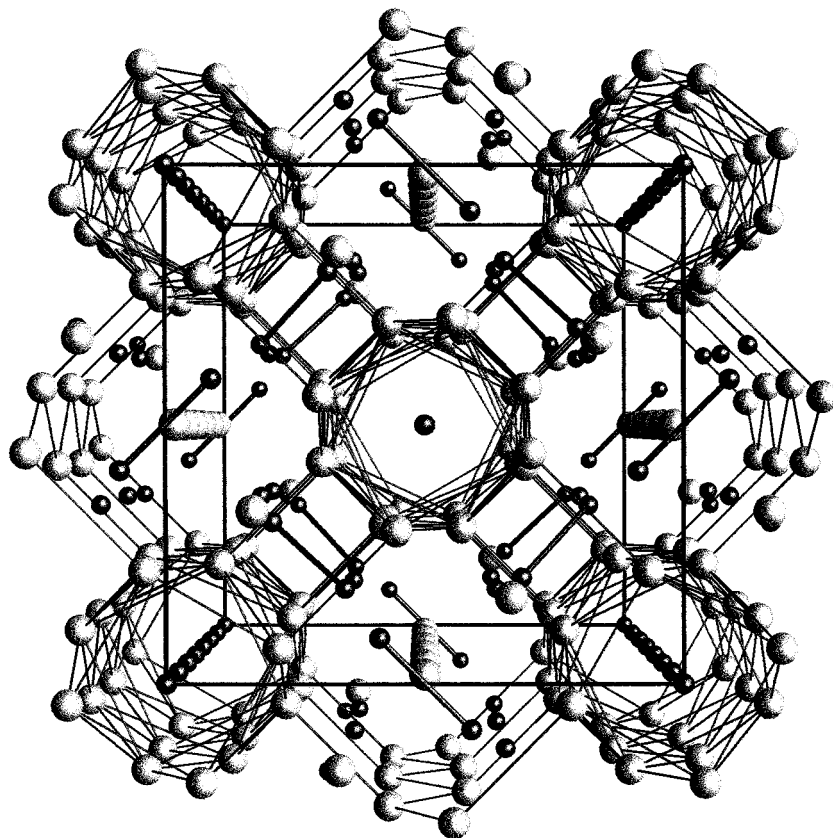


Figure 1. [001] view of the $\text{Yb}_{36}\text{Sn}_{23}$ structure. Small black and large shaded spheres represent Sn and Yb atoms, respectively. Heavier lines denote Sn–Sn bonds while thin lines between Yb atoms only emphasize geometric features. The main feature is chains of confacial, distorted Yb antiprisms along $0,0,z$ and $1/2,1/2,z$ that are centered by tin.

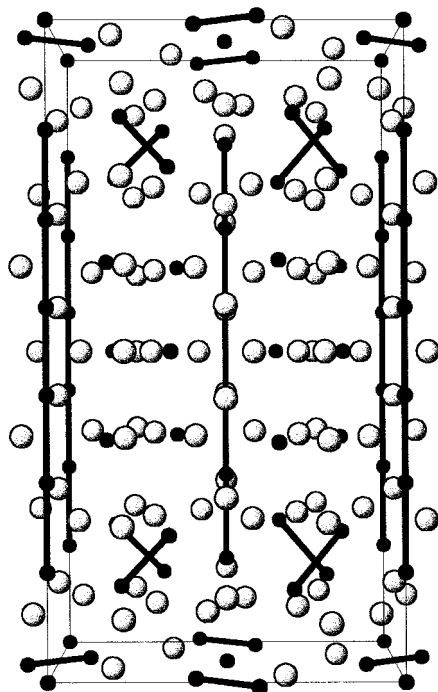


Figure 2. [100] projection of the $\text{Yb}_{36}\text{Sn}_{23}$ structure, with Sn as the smaller solid spheres. Heavy lines emphasize Sn–Sn bonds.

Interatomic distances in the chain are 3.107(5), 3.023(5), 3.046(7), 3.023, and 3.107 Å for Sn2–Sn3–Sn4–Sn4–Sn3–Sn2, respectively (Figure 4a), while Sn–Sn distances of 3.098(7) and 3.156(3) Å occur in the Sn5–Sn5 and Sn7–Sn8 dimers, respectively. The latter are likewise coordinated by a pair of

confacial square antiprisms of Yb. The assumption of formal single bonds between one- and two-bonded tin atoms with distances of 3.02–3.16 Å in $\text{Yb}_{36}\text{Sn}_{23}$ is in good accord with equivalent interactions in $\text{Ca}_{31}\text{Sn}_{20}$ (a diamagnetic semiconductor) at 3.06–3.16 Å. Nominal Sn–Sn single bond interactions in other anionic systems include 3.00 Å for the assumed Sn_2^{6-} in Li_7Sn_2 ,²⁴ 2.94 Å in SrSn^{25} with zigzag chains of $2b\text{-Sn}^{-2}$, 2.84 Å in the dodecahedral network in K_8Sn_{25} , and 2.81 Å in gray tin.³ Both charge repulsions within the polytin anions and matrix effects in this tightly packed structure are expected to play important roles in the bond length variations and increased distances in the oligomeric anions. Thus, the longer $d(\text{Sn7-Sn8})$ appears to correlate with the fact that both Yb4 and Yb7 are positioned so as to restrict the Sn7–Sn8 approach, the distances between Sn8 and Yb4 and Yb7 being the shortest in the structure. Similarly, the longest Sn2–Sn3 bond is at the end of the hexamer chain where there are fairly short Sn2–Yb8 and Sn3–Yb7 contacts as well as an expectation of a greater charge repulsion from the higher formal charge on $1b\text{-Sn}^{2-3}$.

Additional short Sn–Yb contacts occur between Yb3 and Sn6 and Sn9. These are caused by the constrictive tetrahedral coordination around Yb3 in the slab at $z \approx 0.43$, and its equivalent at $z \approx 0.57$. Both are virtually W_5Si_3 -type slabs, and short contacts are generally found between W2 or equivalent atoms that center the edge-sharing tetrahedral chains of Si along $0,1/2,z$, etc. Here, the Yb3-centered edge-sharing bitetrahedral unit formed by Sn6 and Sn9 contains a relatively short Yb3–Yb3 contact, 3.242(4) Å, the darker atoms in Figure 4b, while the rest of the Yb–Yb distances in the structure start at 3.45 Å. The meaning

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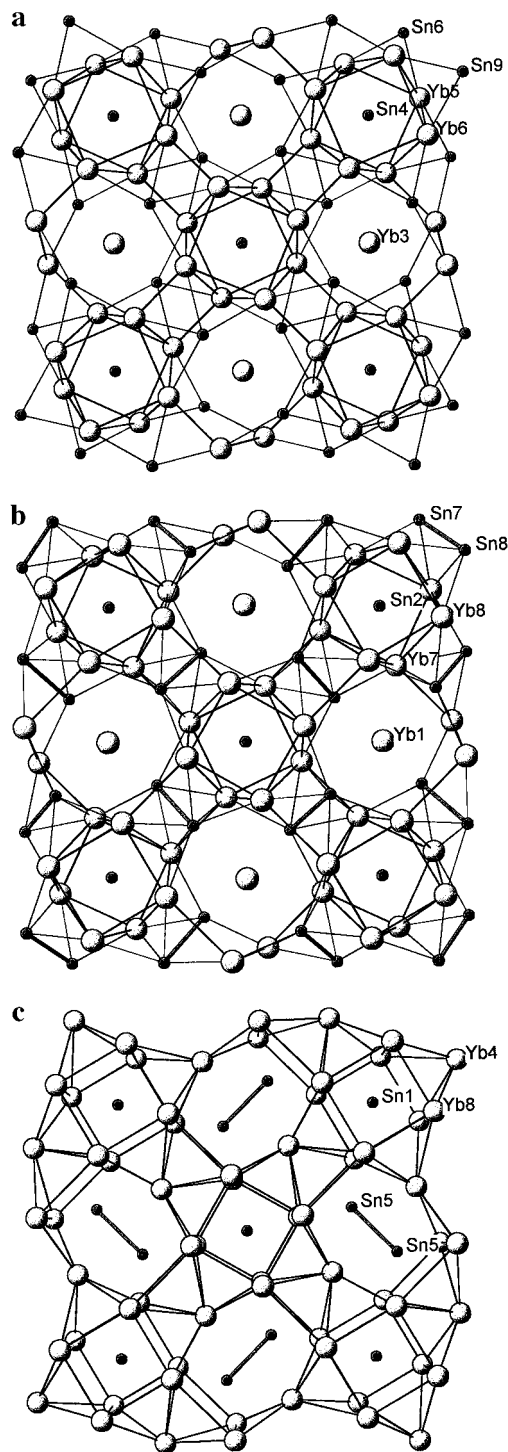


Figure 3. [001] slab sections in $\text{Yb}_{36}\text{Sn}_{23}$. Small solid and large shaded spheres represent Sn and Yb atoms, respectively, with light lines only to aid perspective. (a) W_5Si_3 -like section at $z \approx \pm 0.43$ where Yb5 and Yb6 atoms form the confacial antiprismatic chain centered by Sn4 at $0, 0, 0.43$ etc. and Sn6 and Sn9 atoms centered by Yb3 form the parallel edge-sharing tetrahedral arrangement along $0, \frac{1}{2}, z$ etc. A second more distorted W_5Si_3 -like section at $z \approx \pm 0.30$ is not shown. (b) The distorted slabs around $z \approx \pm 0.17$, showing further twisting of squares in the antiprism of Yb7 and Yb8 that are centered by Sn2, the end member of the Sn_6 unit. Former edge-bridging Sn7 and Sn8 atoms now form dimers. (c) Square prisms centered by Sn1 at $z = 0$ and Sn5–Sn5 dimers in the former tetrahedral columns.

of this closer approach is difficult to judge; it is still 40% greater than twice the Yb crystal radius.²⁶ Questions about a variation in the oxidation state of this cation (or others) on the basis of

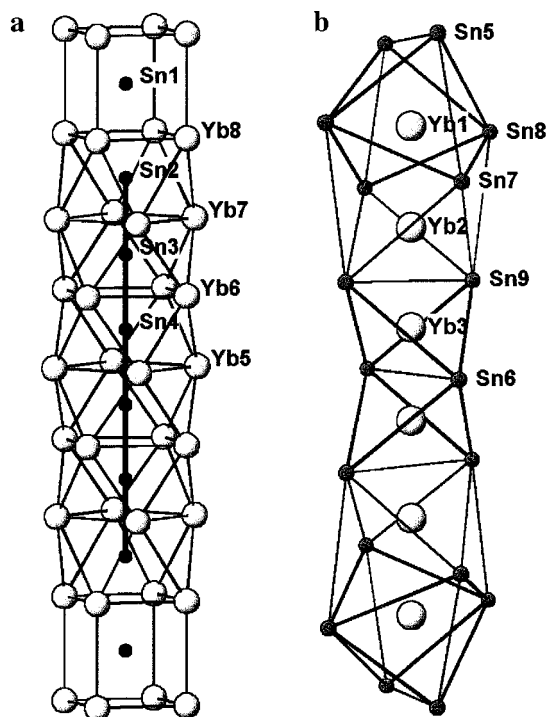


Figure 4. Details of the shared polyhedra in $\text{Yb}_{36}\text{Sn}_{23}$ viewed from the side (\bar{c} vertical). (a) Sequence of centered square prisms and antiprisms of Yb atoms along $0, 0, z$ and $\frac{1}{2}, \frac{1}{2}, z$ with a 1:6 proportion. (b) Yb atoms along $0, \frac{1}{2}, z$, etc. and their Sn coordinations. Heavier lines mark Sn–Sn distances below 5 Å. Yb5 and Sn6 lie on the mirror plane $x, y, \frac{1}{2}$.

properties (below) cannot be disregarded, although all Yb–Sn distances are quite compatible with the presumed divalency of Yb. The averages sort out well according to just the number of Sn about Yb, 3.14–3.23 Å for four neighbors, 3.26–3.41 Å for those with six contacts. There is nothing akin to the 0.16 Å decrease expected were all the cations in one set of equivalent sites to be entirely Yb^{III} .²⁶

Properties. If a classical, localized octet or $8-N$ scheme is applied here,^{2,27} the bonding requirements of tin species match the aggregate for Yb^{II} donors as follows: each hexamer would have a Sn_6^{-14} formulation [four $2b\text{-Sn}^{-2}$ and two $1b\text{-Sn}^{-3}$ (in oxidation states)], while each tin dimer and isolated atom would similarly be described as Sn_2^{-6} and Sn^{-4} , respectively. The 2 hexamers, 10 dimers and 14 isolated tin atoms per cell have an oxidation state sum of -144 , and the 72 Yb^{+2} cations in $\text{Yb}_{36}\text{Sn}_{23}$ ($Z = 2$) make the compound closed shell, that is, a Zintl phase structurally²⁸ (36Yb^{+2} , Sn_6^{-14} , 5Sn_2^{-6} , 7Sn^{-4}) and, in principle, semiconducting and diamagnetic. (Of course, the actual charges are not nearly as large as the assigned oxidation states.)

Electrical resistivity measurements as a function of temperature indicate that $\text{Yb}_{36}\text{Sn}_{23}$ behaves as a poor metal with a room temperature resistivity of $132 \mu\Omega\text{-cm}$ and a temperature coefficient of $0.42(4)\% \text{K}^{-1}$. There are two possible explanations of the conductivity results. Certain cation-deficient compounds with W_5Si_3 -type structures have been observed to have fractional occupation of the W2 position,²⁹ and there is a tight polyhedron

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about the corresponding Yb³⁺ (above). A small deficiency there would either leave open states on the anions or, more likely, be countered by Yb^{III} elsewhere. Along this line, a range of 0.14% (13.6 σ) was observed among the cell volumes refined for five different samples of Yb₃₆Sn₂₃. On the other hand, the resistivity is rather low, and another explanation could well apply. Related Cr₅B₃-type Ae₅Tt₃ phases, which appear to be nominal valence compounds as (Ae⁺²)₅(Tt⁻⁴)Tt₂⁻⁶ (Ae = Ca–Ba, etc.), are often still metallic. Calculations show the expected, that the π^* states of the dimeric Tt₂⁻⁶ are the highest lying, and some delocalization of screened electrons therefrom apparently occurs. In fact, a concomitant shortening of the Tt₂ bond is noted on formal oxidation of some of these phases.^{8,11} The same could easily apply to Sn₂⁻⁶ or Sn₆⁻¹⁴ in Yb₃₆Sn₂₃. Metallic conduction in compounds of this type does not seem so unusual when these involve anionic groups with relatively high formal charges. Many compounds containing polyindium or thallium anion clusters are poor metals even though they are structurally closed shell and diamagnetic,² and some phases with anionic polytin networks are semiconductors and diamagnetic.^{2–6} In any case, one should not lose sight of the fact that the lower lying electrons in bonds are what determine the interesting architecture in these phases, not the behavior of the least bound electrons.

Magnetic susceptibility measurements on two separate preparations of Yb₃₆Sn₂₃ did not afford a lot of information. Both samples appeared to be single phase according to Guinier patterns, but they also had the Yb₅Sn₃ composition used in order to gain a high yield (see Experimental Section). According to the phase diagram,¹² these products should also contain a few percent each of Yb₂Sn + 2Yb impurities. The small magnetism of hcp Yb³⁰ would probably not be evident, and we assume that the unknown magnetic properties of Yb₂Sn could be responsible for the weak paramagnetism and low moments (0.5–0.9 μ_B) deduced from both by nonlinear fitting to the Curie–Weiss expression.³¹ The intrinsic magnetic properties of Yb₃₆Sn₂₃ are thus ambiguous, although a Pauli-like term could be buried in the TIP values found. On the other hand, a small proportion of a mixed valency for some Yb could be responsible for the property observations and yet not be evidenced by Yb–Sn distances.

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(31) Sample 1: TIP = 1.15×10^{-2} emu mol⁻¹, $\theta = -0.7$ K, $\mu_{\text{eff}} = 0.49 \mu_B$. Sample 2: 7.95×10^{-3} emu mol⁻¹, 1.1 K, 0.88, respectively. The Curie–Weiss fits were very good.

Regardless of the detailed nature of Yb₃₆Sn₂₃ and our limited efforts to characterize the properties of this unusual phase, the appearance of this novel result prompts note of how influential very minor changes in cation size or possible electronic effects may be as far as phase stability. The Yb₃₆Sn₂₃ structure has not been found for any other combination of alkaline-earth or divalent rare-earth metal with a tetrel element. The Ca–Sn system would have been anticipated to show some resemblance to the Yb–Sn system, since the standard crystal radius of Ca²⁺ is only ca. 1.7% (0.02 Å) smaller than that of divalent Yb²⁺,²⁶ and the two show parallel chemistries in many pnictide system, e.g., as both A₅Pn₃¹⁰ and A₁₆Pn₁₁⁹ for A = Ca, Yb with Pn = Sb or Bi. On the other hand, we have found that Ca–Sn reactions at about a 5:3 proportion (and low hydrogen concentrations) lead to the formation of only the other oligomeric structure Ca₃₁Sn₂₀. The replacement of Sn by Pb in both Yb and Ca reactions likewise leads to Yb₃₁Pb₂₀ and to an incompletely characterized superstructure of a Mn₅Si₃-like compound,^{8,32} respectively. This sensitivity of the formation of the present $n = \text{six}$ member of Parthé's homologous series to cation size also hints that possible higher members may be attained with careful attention to reaction partner properties.

It is remarkable how novel new phases can still be found in supposedly well-studied binary systems, as for Yb₃₆Sn₂₃. Obscuring effects from impurity hydrogen appear to have played an important role in precluding an earlier discovery of this phase. Several compounds with the Cr₅B₃-type structure reported to be formed at approximately the same composition are now known to be hydrides, e.g., Yb₅Sn₃H.^{8,11} Hydrogen effects are not unique to this composition; our experimental results strongly suggest that the “binary” Yb₅Sn₄ may be a hydrogen-stabilized compound as well. Additional results from our studies of such polar intermetallic compounds will be the subjects of further reports.¹¹

Acknowledgment. We thank J. Ostenson for the magnetic susceptibility measurements.

Supporting Information Available: Tables of additional data collection and refinement information and a listing of the anisotropic displacement parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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