

[Hg₇As₄I₃](SnI₃): Trapping the SnI₃¹⁻ Anion in the Cavities of the Unprecedented Mercury-Arsenic-Iodine Network

Andrei V. Oleney,^[a] Alexei I. Baranov,^[b] Andrei V. Shevelkov,^{*[a]} and Boris A. Popovkin^[a]

Keywords: Host–guest compounds / Tin / Mercury / Pnictide halides

A novel host–guest compound [Hg₇As₄I₃](SnI₃) has been prepared by a standard ampoule technique and its crystal structure was determined. It crystallizes in a cubic system [space group *P*2₁3, *a* = 13.110(1) Å, *Z* = 4] with a unique structure type. The crystal structure comprises two parts: the three-dimensional [Hg₇As₄I₃]¹⁺ host network, and the SnI₃¹⁻ guest anions encapsulated in the cavities of the network. The network is built from the As₂Hg₇ bitetrahedra and As₂Hg₆

octahedra, which share corners, and contains an additional iodine atom connected to one of the mercury vertices. The SnI₃¹⁻ anion has the shape of a pyramid with the tin atom in a vertex. According to the quantum-chemistry calculations, the geometry of the anion deviates substantially from the equilibrium one, and is influenced by the distant mercury atoms of the host network.

Introduction

The rapidly developing field of inorganic supramolecular chemistry covers a large diversity of compounds, and classes of compounds, the important feature of which is a weak interaction between host and guest units.^[1] In most cases, electrically neutral hosts and guests constitute supramolecular compounds, and their interaction is normally limited to van der Waals forces. However, in compounds where hosts and guests are electrically charged, weak electrostatic host–guest interaction is expected. The “weakness” of such an interaction is sometimes illustrated by the positional and/or rotational disorder of small guest anions encapsulated in host structures, but perfectly ordered structures are not rare cases.^[2]

A number of inorganic supramolecular compounds containing linearly coordinated mercury in the host substructures has been reported in the literature.^[3–10] Apart from 2HgS·SnBr₂,^[3] a unique one-dimensional host–guest compound, all mercury-based supramolecular compounds comprise charged guests and hosts. Hg₂VO₄ is the exception and contains the Hg₂²⁺ cations in the host network.^[4] In all other compounds, hosts are three-dimensional cationic networks, based on divalent mercury atoms linearly coordinated by Group-15 elements. Two principal types of networks can be distinguished in these compounds according to the dimension of the voids. Channels are the characteristic feature of the Millon's base salts^{[5][6]} and their phosphorus and arsenic analogs,^{[7][8]} while closed cavities form in highly symmetric mercury pnictide halides, such as [Hg₆As₄](HgCl₆)Hg_{0.4} and related cases.^{[9][10]} Different types of positional disorder of guest anions are frequently

observed in both types of compounds, indicating the weakness of the host–guest interaction.^[5,8–10]

The structure of host networks and the size of the voids are primarily controlled by the nature and coordination demands of the elements composing the network. In all mercury/pnictogen networks, linearly coordinated mercury atoms alternate with tetrahedrally coordinated pnictogen atoms. Pnictogens, other than nitrogen, adopt a tetrahedral coordination in any oxidation state, and at least two of them, –2 and –3, are displayed in supramolecular mercury pnictide halides.^[7–10] In the –2 oxidation state, pnictogens form Z₂⁴⁻ dumbbells, which substantially influence the size of the voids; the greater the number of dumbbells, the smaller the size.^[8] Therefore, the size of the voids does not necessarily increase on going from nitrogen to antimony. The second factor that controls the size of the voids is the nature and the size of the guest. The latter can serve as a template, and the network forms around it in the course of the synthesis. In recent work^[8] we have shown that decreasing the size of the tetrahedral anion ZnX₄²⁻ from X = I to X = Cl leads to the Hg/As networks with decreasing size of the voids; and the adjustment of the network dimensions to the size of the anions occurs through a formation of the As–As bonds.

In the course of our research, aimed at the preparation of new host–guest compounds based on a mercury–pnictogen framework, we attempted the synthesis of [Hg₆As₄](SnI₆)Hg. Taking into account the ease of suppressing the Sn^{II} lone electron pair in the iodine environment,^[11] we expected to obtain an ordered analog of a supramolecular compound [Hg₆As₄](HgCl₆)Hg_{0.4}.^[10] The latter possesses a 3D cationic network, [Hg₆As₄]⁴⁺, with voids of different sizes. The larger cavities are filled with regular octahedral anions (HgCl₆)⁴⁻, while the smaller cavities are partially (40%) filled by zero-valent mercury atoms. Surprisingly, another new compound, [Hg₇As₄I₃](SnI₃), having a unique crystal structure, but the same overall composition as the target phase, was obtained. In this article we report

^[a] Inorganic Synthesis Laboratory, Department of Chemistry, Moscow State University, Leninskie Gory, Moscow 119899, Russia
Fax: (internat.) + 7-095/939-4788
E-mail: shev@inorg.chem.msu.ru

^[b] High School for Material Sciences, Moscow State University

the synthesis and crystal structure of a novel supramolecular compound $[\text{Hg}_7\text{As}_4\text{I}_3](\text{SnI}_3)$. The influence of the charged host network on the geometry of the guest $(\text{SnI}_3)^{1-}$ anion is analyzed based on the quantum-chemistry *ab initio* calculations.

Results and Discussion

Synthesis and X-ray Study

$[\text{Hg}_7\text{As}_4\text{I}_3](\text{SnI}_3)$ was obtained from a stoichiometric mixture of mercury, arsenic, tin, and mercury diiodide by a standard two-step ampoule synthesis at 670 K over 10 d. The almost single-phase product appears as a black polycrystalline, air-stable bulk sample, dark-brown after fine grinding. After accounting for the weak admixture reflections, an X-ray pattern taken from the sample was indexed in a primitive cubic cell with a unit cell edge $a = 13.1117(6)$ Å (Guinier data). Single crystals suitable for the structure determination were prepared by annealing the starting materials mixed in a 2:2:1:2 ratio at 670 K for 1 week in a sealed silica ampoule. The crystal structure was refined based on single-crystal X-ray data (Table 1). The refinement confirms both crystal system and composition.

Table 1. Data collection and structure refinement parameters for $[\text{Hg}_7\text{As}_4\text{I}_3](\text{SnI}_3)$

Empirical formula	$\text{As}_4\text{Hg}_7\text{I}_6\text{Sn}$
Space group	$P2_13$ (No. 198)
Cell parameter a [Å]	13.110(1)
V [Å ³]	2253.2(3)
Z	4
Density (calcd.) [g cm ⁻³]	7.617
μ [1/mm]	62.624
Crystal size [mm]	$0.25 \times 0.10 \times 0.05$
Radiation, λ [Å]	Mo- K_α , 0.71069
Data collection range [°]	$2.20 < \theta < 25.97$
Reflections collected	2715
Independent refl.	1013 ($R_{\text{int}} = 0.1444$)
Parameters refined	56
R_1 , wR_2 ^[a] [$F_o > 4\sigma(F_o)$]	0.0464, 0.0940
R_1 , wR_2 (all data)	0.0668, 0.1020
Largest diff. peak and hole [$e/\text{Å}^3$]	2.208, -2.392
G.o.f. on F^2	1.079

^[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + 0.0310(F_o^2 + 2F_c^2)/3]^{-1}$.

Description of the Crystal Structure

Atomic positions, equivalent isotropic displacement parameters, and selected bond lengths and valence angles are summarized in Tables 2 and 3. Two parts of the crystal structure of $[\text{Hg}_7\text{As}_4\text{I}_3](\text{SnI}_3)$ can be subtracted: a $[\text{Hg}_7\text{As}_4\text{I}_3]^{1+}$ positively charged framework and $(\text{SnI}_3)^{1-}$ anions, which are encapsulated in the cavities of the framework (Figure 1). The $(\text{SnI}_3)^{1-}$ anion comprised of the unique tin and I(2) atoms has a shape of a trigonal pyramid with the tin atom at the vertex, the Sn–I distances and I–Sn–I angles being 2.95 Å and 90.97°, respectively. Surprisingly, we have not found any data on such an anion in

literature, although the analogous $(\text{SnCl}_3)^{1-}$ anion with the same shape has been observed in various compounds.^[12]

Table 2. Atomic parameters for $[\text{Hg}_7\text{As}_4\text{I}_3](\text{SnI}_3)$

Atom	Wyckoff	x/a	y/b	z/c	$U_{\text{eq}}^{[a]}$ 10 ⁻⁴
Hg(1)	4a	0.0342(1)	0.0342(1)	0.0342(1)	25(1)
Hg(2)	12b	0.0930(1)	0.0726(1)	0.3143(1)	23(1)
Hg(3)	12b	0.5677(1)	-0.0007(1)	0.2488(1)	25(1)
I(1)	12b	0.9696(2)	0.2585(2)	0.8181(2)	25(1)
I(2)	12b	0.1856(2)	0.0543(2)	0.7889(2)	21(1)
Sn	4a	0.7671(2)	0.7671(2)	0.7671(2)	26(1)
As(1)	4a	0.9258(2)	0.9258(2)	0.9258(2)	12(1)
As(2)	4a	0.1428(2)	0.1428(2)	0.1428(2)	11(1)
As(3)	4a	0.4315(2)	0.4315(2)	0.4315(2)	10(1)
As(4)	4a	0.5370(2)	0.5370(2)	0.5370(2)	11(1)

^[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

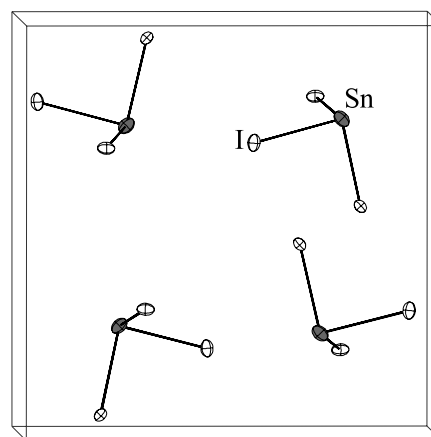
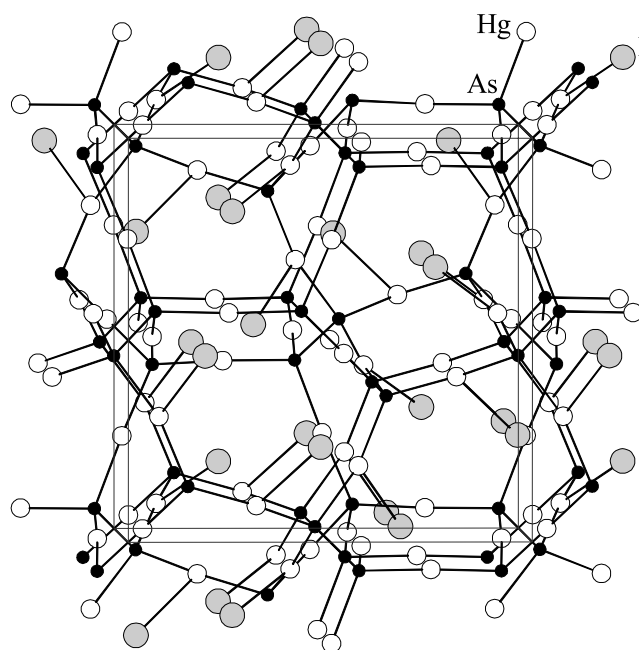


Figure 1. Building units of the crystal structure of $[\text{Hg}_7\text{As}_4\text{I}_3](\text{SnI}_3)$; a fragment of the $[\text{Hg}_7\text{As}_4\text{I}_3]^{1+}$ framework (top) and a distribution of the $(\text{SnI}_3)^{1-}$ within the unit cell (bottom)

The 3D cationic net is built of the arsenic, mercury, and one of two nonequivalent iodine atoms. Three independent mercury atoms have almost the same linear coordination of two arsenic atoms. While the coordination of the Hg(1) atom is regular, the As–Hg–As angle deviates from 180° for the Hg(2) and Hg(3) atoms. Clearly, a rather distant (3.16 Å) iodine neighbor, the I(1) atom, which we consider to belong to the cationic net, causes the departure from linearity in the case of the Hg(2) atom. The Hg–I separation of 3.16 Å is noticeably longer than the covalent interactions in all three forms of HgI₂ (2.62–2.78 Å),^[13] but is only slightly longer than the Hg–I distances in various mercury pnictide iodides (3.03–3.14 Å).^[14]

Four independent arsenic atoms have a tetrahedral coordination of two different types. The As(1) and As(2) atoms are surrounded by four mercury atoms. These two tetrahedra are connected through the common Hg(1) atom, forming a bitetrahedral As₂Hg₇ unit (Figure 2). The As(3) and As(4) atoms are joined in an As–As dumbbell, and each of them completes its tetrahedral coordination with three mercury atoms. Six mercury atoms thus surround the dumbbell, forming an As₂Hg₆ octahedron (Figure 2). The bitetrahedra and octahedra share vertices to compose the cationic net, the polyhedral presentation of which is drawn in Figure 3. It should be mentioned that the analogous building blocks, the P₂Hg₆ octahedra and P₂Hg₇ bitetrahedra, are found in Hg₉P₅I₆,^[15] which, however, possesses another type of crystal structure.

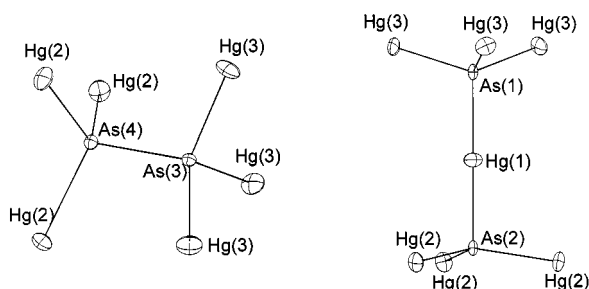


Figure 2. Coordination of the arsenic atoms in [Hg₇As₄I₃](SnI₃) (50% probability ellipsoids)

The As–As separation of 2.40 Å is usual for numerous pnictide halides containing As₂⁴⁻ anions.^[8,10,16,17] It falls in the range of 2.37–2.43 Å, where the shortest and longest distances refer to Hg₄As₂Br₃^[10] and Hg₁₉As₁₀Br₁₈,^[17] respectively. The As–Hg distances (2.46–2.53 Å) are also typical for the mercury arsenide halides,^[8,10,17] and do not depend much on the formal oxidation state of the arsenic atoms, –3 for As(1) and As(2), and –2 for As(3) and As(4). The absence of the Hg–Hg bonds indicates that the oxidation state +2 can be assigned to the mercury atoms, and hence the crystallographic formula [(Hg²⁺)₇(As³⁻)₂(As₂⁴⁻)(I¹⁻)₃](SnI₃)¹⁻ can be derived for the title compound. The formula reflects an unusual composition of the cationic network. To our knowledge, it is the second example of the mercury-based supramolecular compound, which has a halogen atom as a part of the cationic net. A host–guest compound [Hg₉As₄Br₂](Bi₂Br₁₀)

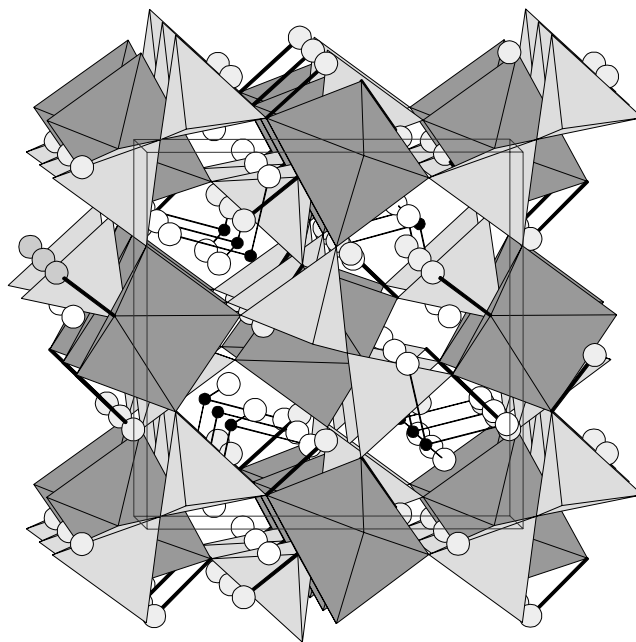


Figure 3. A polyhedral presentation of the crystal structure of [Hg₇As₄I₃](SnI₃); polyhedra: As₂Hg₆ octahedra, dark gray; As₂Hg₇ bitetrahedra, light gray; atoms: tin, filled circles; I(1), shaded circles; I(2), open circles

has been reported^[18] to contain two bromine atoms per network formula.

Theoretical Study of SnI₃¹⁻

The SnI₃¹⁻ anion encapsulated in the closed cavities of the three-dimensional network exhibits a geometry well predicted by the Gillespie–Nyholm rules.^[19] Qualitatively, one can expect a pseudo-tetrahedral arrangement of three iodine atoms and one lone electron pair around the Sn²⁺ cation in an isolated (SnI₃)¹⁻ anion, with I–Sn–I angles being lower than regular tetrahedral ones. The Extended Hückel^[20] calculations, performed on the anion having the geometry found from the structure refinement, show (Figure 4) that the 4a₁ orbital, the HOMO, has the greatest contribution from the tin 5s and 5p_z atomic orbitals. These orbitals interact slightly with the iodine 5p orbitals (namely, 5p_z orbitals if each iodine atom resides on its local coordinate system with z axis pointing to the tin atom). The resulting orbital, the HOMO, can be considered as a lone electron pair, as visualized in Figure 5.

The anion trapped in the 3D cationic net, however, may feel the influence of the charged net. While the Sn–I(1) separation is rather distant (3.63 Å), the I(2) atom, which belongs to the anion, lies not very far from three mercury atoms, which belong to the cationic framework. The respective distances of 3.36–3.43 Å significantly exceed the sum of the respective covalent radii, but are even shorter than the longest Hg–I separation of 3.51 Å observed in the structure of the yellow modification of HgI₂.^[13] Thus, a slight “host–guest” interaction is expected to affect the geometry of the anion under consideration. To obtain the

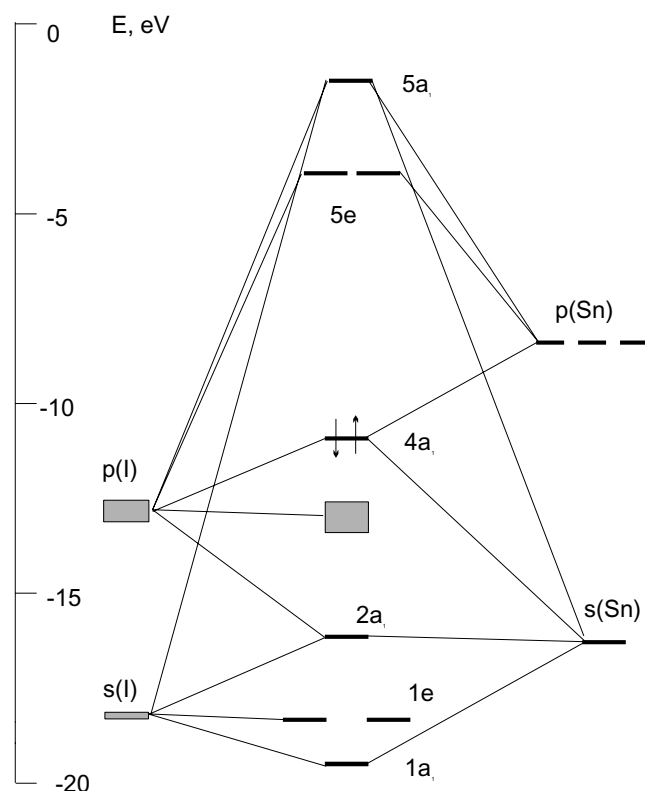


Figure 4. The Extended Hückel molecular orbital diagram for the $(\text{SnI}_3)^{1-}$ anion in $[\text{Hg}_7\text{As}_4\text{I}_3](\text{SnI}_3)$; mainly nonbonding orbitals in the energy range of -13.3 to -12.5 eV, localized on the iodine atoms, are shown as a dashed box

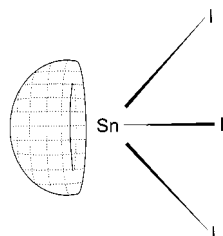


Figure 5. The shape of the $4a_1$ orbital (HOMO) of the isolated $(\text{SnI}_3)^{1-}$ anion from the Extended Hückel calculations

equilibrium geometry of $(\text{SnI}_3)^{1-}$, quantum-chemistry ab initio RHF calculations^[21] were performed. The geometry of the $(\text{SnI}_3)^{1-}$ anion was optimized with both Sn–I bond lengths frozen at $d(\text{Sn}–\text{I}) = 2.95$ Å (C_{3v} symmetry) and without any constraints (C_{3v} and C_s symmetries). Constraint-free calculations converged at 2.900 Å Sn–I bond length and 99.18° I–Sn–I bond angle. These values deviate significantly from 2.952(3) Å and 90.9(1)° found from the structure refinement. Only marginal geometry differences were encountered between anions optimized in the C_s and C_{3v} point groups. Optimization with the frozen Sn–I bond length resulted in less than 0.2° I–Sn–I angle difference with the fully optimized ion. The results of the calculations can be explained with the help of Figure 6, which shows the arrangement of the distant mercury atoms of the network around the $(\text{SnI}_3)^{1-}$ anion. The observed $(\text{SnI}_3)^{1-}$ anion exhibits a Sn–I bond length 0.05 Å longer than the equilib-

rium bond length, and such an elongation indicates a slight bonding interaction of the iodine atoms with the mercury atoms. Evidently, the almost 9° difference in the I–Sn–I bond angle is also caused by the same I–Hg interaction, since the optimization with the Sn–I distance frozen at 2.95 Å gives the same I–Sn–I angle as the full optimization. Therefore, the observed I–Sn–I bond angle value of 90.9° is obviously a result of the “combined influence” (a vector sum) of nine mercury atoms on the anion under consideration.

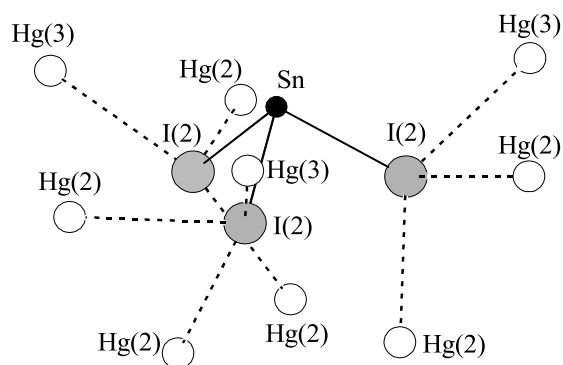
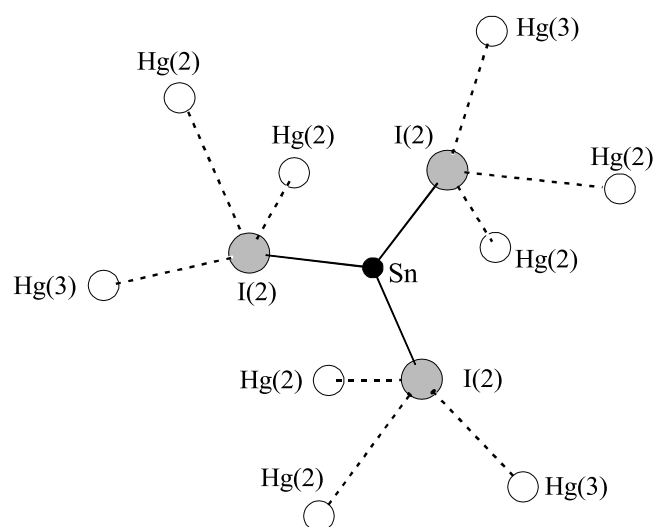


Figure 6. Arrangement of the distant mercury atoms around the $(\text{SnI}_3)^{1-}$ anion in the structure of $[\text{Hg}_7\text{As}_4\text{I}_3](\text{SnI}_3)$: a) a view along the 3-fold axis; b) a side-view almost along a (011) direction of the unit cell

Conclusions

$[\text{Hg}_7\text{As}_4\text{I}_3](\text{SnI}_3)$ is a novel host–guest compound possessing two interesting structural features. Firstly, the cationic network is composed not only of mercury and arsenic, but also iodine atoms. Secondly, the closed cavities are filled with the $(\text{SnI}_3)^{1-}$ anions, which have never been observed as guest units in supramolecular compounds. The positions

of the SnI₃¹⁻ anions within the unit cell are accurately determined; no sign of positional and/or rotational disorder has been observed during the structure refinement. Together with deviation of the observed anion geometry from that at equilibrium, this indicates the existence of a weak host–guest interaction in the title compound, the nature of which was not investigated in this work. However, such an interaction seems to be very important in the formation of compounds. Evidently, being isolated from each other in the closed cavities of the 3D network, the anions cannot exhibit ion exchange, nor can they enter the well-formed net. The net itself carries a positive charge, and hence cannot exist without anionic guests. Consequently, the title compound can only form spontaneously during the synthesis through a self-assembly process.

Experimental Section

Synthesis: Liquid mercury, gray arsenic, tin powder and mercury diiodide (all > 99.9% purity) were mixed in a 4:4:1:3 molar ratio. The mixture (1 g) was vacuum-sealed in a silica tube and annealed for 10 d at 670 K with intermediate grinding. An X-ray analysis (Guinier FR-552, Nonius) of the product revealed traces of unchanged starting materials, while most reflections belonged to a new phase. The corresponding reflections were indexed in a cubic system with a unit cell parameter $a = 13.1117(6)$ Å. For the single-crystal preparation, the starting materials were mixed in a molar ratio 2:2:1:2 and vacuum-sealed in a silica tube, 60 mm in length and 7 mm inner diameter. The ampoule was placed in a vertical furnace, heated slowly (30°/h) to 670 K and exposed to this temperature for 1 week. After cooling to room temperature at 30°/h, well-formed black crystals were found all over the ampoule. The crystals were separated mechanically, and an X-ray analysis confirmed them to be the desired phase.

Crystal Structure Determination: A suitable single crystal ($0.25 \times 0.1 \times 0.05$ mm) was selected from the sample and mounted on a CAD-4 (Nonius) goniometer head for structure investigation. A cubic unit cell parameter $a = 13.110(1)$ Å was refined based on 24 well-centered reflections in the angular range $10.56^\circ < \theta < 13.47^\circ$. Data were collected at ambient temperature in the ω -2 θ scan mode with data collection parameters listed in Table 1. A semi-empirical absorption correction was applied to data based on ψ -scans of 6 reflections having their χ angles close to 90° . Analysis of systematic reflection conditions showed that two space groups $P2_13$ (No. 198) and $P4_232$ (No. 208) were the possibilities. The refinement was successful in the lower symmetry space group $P2_13$. Positions of mercury, tin and iodine atoms were found by direct methods. Arsenic atoms were localized by a sequence of $\Delta\rho(xyz)$ syntheses and least square cycles. The final anisotropic refinement on F^2 led to $R_1 = 0.0464$ and $wR_2 = 0.0939$. All calculations were carried out using SHELX97 programs.^[22] Further details of the crystal structure determination may be obtained from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-410814.

Computational Aspects: Extended Hückel calculations were carried out on the (SnI₃)¹⁻ anion, with the geometry found from the crystal structure refinement (Table 3) using CACAO program.^[23] Atomic orbital parameters were taken from the literature.^[24] Ab initio RHF calculations were performed using GAMESS-US program. SBKJC effective core potentials applied to all atoms and SBKJC basis set^[25] implemented in GAMESS were used. Starting

geometry of the (SnI₃)¹⁻ was taken from the crystal structure refinement. Geometry optimizations were performed by the quasi-Newton algorithm^[26] implemented in GAMESS. The followed Hessian computation and normal vibration analysis showed all stationary points located to be minima.

Table 3. Selected interatomic distances and bond angles for [Hg₇As₄I₃](SnI₃)

Distances [Å]	
Sn–I(2)	2.952(3) × 3
As(1)–Hg(1)	2.462(6)
As(1)–Hg(3)	2.520(2) × 3
As(2)–Hg(1)	2.466(6)
As(2)–Hg(2)	2.515(2) × 3
As(3)–Hg(3)	2.526(2) × 3
As(4)–Hg(2)	2.530(2) × 3
As(3)–As(4)	2.397(7)
Hg(2)–I(1)	3.160(3)
Hg(3)–I(1)	3.308(3)
Hg(2)–I(2)	3.362(2)
Hg(2)–I(2)	3.431(2)
Hg(3)–I(2)	3.435(2)
Angles [°]	
I(2)–Sn–I(2)	90.87(11) × 3
Hg(1)–As(1)–Hg(3)	106.69(12) × 3
Hg(3)–As(1)–Hg(3)	112.11(11) × 3
Hg(1)–As(2)–Hg(2)	98.91(13) × 3
Hg(2)–As(2)–Hg(2)	117.65(7) × 3
Hg(3)–As(3)–Hg(3)	109.40(12) × 3
Hg(2)–As(4)–Hg(2)	112.26(11) × 3
As(3)–As(4)–Hg(2)	106.51(12) × 3
As(4)–As(3)–Hg(3)	109.54(12) × 3
As(1)–Hg(1)–As(2)	180.0(3)
As(2)–Hg(2)–As(4)	166.29(15)
As(1)–Hg(3)–As(3)	176.84(14)

Acknowledgments

Authors wish to thank Dr. A. N. Kuznetsov for helpful discussion. This work was supported by the state program “Universities of Russia”.

- [1] A. Müller, H. Reuter, S. Dillinger, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2328; *Angew. Chem.* **1995**, *107*, 2505.
- [2] [2a] P. N. W. Baxter, J.-M. Lehn, B. O. Kneisel, G. Baum, D. Fenske, *Chem. Eur. J.* **1999**, *5*, 113. – [2b] P. N. W. Baxter, J.-M. Lehn, G. Baum, D. Fenske, *Chem. Eur. J.* **1999**, *5*, 102. – [2c] W. Schnick, J. Lücke, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 213; *Angew. Chem.* **1992**, *104*, 208.
- [3] R. Blachnik, K. Lytze, H. Reuter, *J. Solid State Chem.* **1996**, *126*, 95.
- [4] A. L. Wessel, W. Jeitschko, *J. Solid State Chem.* **1996**, *125*, 140.
- [5] W. Ruedorf, K. Brodersen, *Z. Anorg. Allg. Chem.* **1953**, *274*, 223.
- [6] L. Nijssen, W. N. Lipscomb, *Acta Crystallogr.* **1954**, *7*, 103.
- [7] A. V. Shevelkov, M. Yu. Mustyakimov, E. V. Dikarev, B. A. Popovkin, *J. Chem. Soc., Dalton Trans.* **1996**, *1*, 147.
- [8] A. V. Olenov, A. V. Shevelkov, B. A. Popovkin, *Zh. Neorg. Khim.*, in press.
- [9] A. V. Shevelkov, E. V. Dikarev, B. A. Popovkin, *J. Solid State Chem.* **1992**, *98*, 133.
- [10] A. V. Shevelkov, E. V. Dikarev, B. A. Popovkin, *J. Solid State Chem.* **1996**, *126*, 324.
- [11] [11a] R. A. Howie, W. Moser, I. C. Trevena, *Acta Crystallogr. B.* **1972**, *28*, 2965. – [11b] K. Yamada, S. Funabiki, H. Horimoto,

- T. Matsui, T. Okuda, S. Ishiba, *Chem. Lett.* **1991**, 801. — [11c] H. P. Beck, W. Thiel, M. Schuster, *Z. Anorg. Allg. Chem.* **1993**, 619, 221.
- [12] For example, see [12a] CsSnCl₃: F. R. Poulsen, S. E. Rasmussen, *Acta Chem. Scand.* **1970**, 24, 150. — [12b] [Co(CO)₄]SnCl₃: P. Klüfers, *Z. Naturforsch. B* **1991**, 46, 187.
- [13] A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Oxford, Clarendon Press, **1984**, chapter 26.
- [14] [14a] P. Labbé, M. Ledésert, B. Raveau, A. Rebbah, *Z. Kristallogr.* **1989**, 187, 117. — [14b] A. V. Shevelkov, E. V. Dikarev, B. A. Popovkin, *J. Solid State Chem.* **1991**, 93, 331. — [14c] A. V. Shevelkov, E. V. Dikarev, B. A. Popovkin, *Z. Anorg. Allg. Chem.* **1994**, 620, 389.
- [15] M. Ledésert, A. Rebbah, Ph. Labbé, *Z. Kristallogr.* **1990**, 192, 223.
- [16] A. Rebbah, J. Yazbeck, A. Leclaire, A. Deschanvres, A. Leclaire, A. Deschanvres, *Acta Crystallogr. B* **1980**, 36, 771.
- [17] A. V. Shevelkov, E. V. Dikarev, B. A. Popovkin, *Zh. Neorg. Khim.* **1995**, 40, 1496; *Chem. Abstr.* **1995**, 123, 905020e.
- [18] H. Puff, M. Grönke, B. Kilger, P. Möltgen, *Z. Anorg. Allg. Chem.* **1984**, 518, 120.
- [19] R. J. Gillespie, I. Hargittai, *The VSEPR Model of Molecular Geometry*, Allyn and Bacon, Boston, **1991**.
- [20] J. H. Ammeter, H. B. Bürgi, J. C. Thibaut, R. Hoffmann, *J. Am. Chem. Soc.* **1978**, 100, 3686.
- [21] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, J. A. Montgomery, *J. Comput. Chem.* **1993**, 14, 1347.
- [22] [22a] G. M. Sheldrick, *SHELXS-97, Program for crystal structure solution*, University of Göttingen, Germany, **1997**. — [22b] G. M. Sheldrick, *SHELXL-97, Program for crystal structure refinement*, University of Göttingen, Germany, **1997**.
- [23] C. Mealli, D. M. Proserpio, *J. Chem. Educ.* **1990**, 67, 3399.
- [24] P. Pykkö, L. L. Lohr, Jr., *Inorg. Chem.* **1981**, 20, 1950.
- [25] [25a] W. J. Stevens, H. Basch, M. Krauss, *J. Chem. Phys.* **1984**, 81, 6026. — [25b] W. J. Stevens, H. Basch, M. Krauss, P. Jasien, *Can. J. Chem.* **1992**, 70, 612. — [25c] T. R. Cundari, W. J. Stevens, *J. Chem. Phys.* **1993**, 98, 5555.
- [26] J. Baker, *J. Comput. Chem.* **1986**, 7, 385.

Received June 6, 1999
[199214]