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First Tin Pnictide Halides $Sn_{24}P_{19.3}I_8$ and $Sn_{24}As_{19.3}I_8$: Synthesis and the Clathrate-I Type of the Crystal Structure

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$Sn_{24}P_{19.3}I_8$ (**I**) and $Sn_{24}As_{19.3}I_8$ (**II**) have been prepared by a standard ampule synthesis. **I** crystallizes in a cubic space group $Pm\bar{3}n$, $a = 10.9540(10)$ Å, $z = 1$. The crystal structure of **I** is built of the 3D net composed of tin and phosphorus atoms, while iodine atoms occupy large polyhedral holes of two different types, pentagonal dodecahedral and tetrakaidodecahedral. An arrangement of such polyhedra follows that of the clathrate-I type. The 3D net has vacancies at one of the phosphorus atoms positions. The vacancies cause the split of the tin atomic position into two, having different coordination, which is reflected in the ^{119}Sn Mössbauer spectrum. The vacancy concentration correlates well with the occupancy factors of the split tin atomic positions, and in accordance with the Zintl−Klemm formalism for valence compounds, **I** is a narrow-gap semiconductor. Powder diffraction data shows that **II** belongs to the same clathrate family, but has an 8 times larger face-centered cubic unit cell.

Introduction

About 20 years ago von Schnering and Menke[1] prepared a family of compounds with a general formula $Ge_{38}E_8I_8$ (E = P, As, Sb). They all belong to the clathrate-I class according to their crystal structures, where four-coordinated germanium and pnictogen atoms compose a three-dimensional net. The oxidation states of the atoms in these compounds, except for iodine, are uncertain, that is reflected by the formulation $(Ge_{38}E_8)^{8+}(I^-)_8$. No analogues of these compounds, e.g., with either silicon or tin instead of germanium, are known. It is likely, that tin would be in the oxidation state +2 in tin pnictide halides, and form structures related to the common mercury and cadmium pnictide halides,[2] and recently[3] we have shown that in the latter compounds tin substitutes for cadmium. However, our attempts to prepare tin analogues of the cadmium pnictide halides resulted in a preparation of $Sn_{24}P_{19.3}I_8$ (**I**) and $Sn_{24}As_{19.3}I_8$ (**II**), which, having formulas different from those of germanium compounds, belong to the same clathrate-I type; their syntheses and the crystal structure of **I** are reported in this article.

Experimental Section

Starting Materials. Tin pellets, arsenic powder, and crystalline iodine, all of high purity (≥99.99%) were used as received. Red phosphorus (99.7%) was washed before use consequently with 10% aqueous solution of KOH, water, ethanol (twice) and vacuum-dried. Tin tetraiodide was prepared by a standard procedure.[4]

Table 1. Crystallographic Data for **I**

chem formula $I_8P_{19.29}Sn_{24}$	fw 4461.17
$a = 10.9540(9)$ Å	sp gr $Pm\bar{3}n$ (No. 223)
$V = 1314.4(2)$ Å	$T = 21$ °C
$Z = 1$	$\lambda = 0.710\ 69$ Å
$R(F_o)^a = 0.0260$	$\rho_{calcd} = 6.636$ g cm^{-1}
$wR(F_o2)^b = 0.0540$	$\mu = 16.463$ mm^{-1}

[a] $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o||$. [b] $wR(F_o^2) = [\sum w(F_o^2 - F_c^2)^{1/2}/\sum w(F_o^2)^{1/2}]^{1/2}$, $w = [\sigma^2(F_o^2) + 4.7116(F_o^2 + 2F_c^2)/3]^{-1}$.

Synthesis of $Sn_{24}P_{19.3}I_8$ (I) and $Sn_{24}As_{19.3}I_8$ (II). I and **II** were each prepared by a standard ampule technique. For this, the respective stoichiometric mixtures of tin, tin tetraiodide, and phosphorus or arsenic (total weight 1 g) were vacuum-sealed in silica tubes (50 mm length, 6 mm inner diameter) and heated at 773 K for 5 days. After regrinding, the samples were heated in sealed silica tubes at 773 K for 14 days. The products appeared as black polycrystalline moisture-resistant powders. An X-ray analysis (Nonius FR-552 camera, Cu $K\alpha_1$ radiation) did not detect traces of starting materials.

For the single-crystal preparation of **I**, a mixture of tin, phosphorus, and tin tetraiodide in a molar ratio 15:12:1 was annealed in a sealed silica tube at 773 K for 5 days. During that period well-shaped cubooctahedral black crystals have grown all over the ampule. Attempts to prepare single crystals of **II** suitable for the structure determination failed.

X-ray Characterization. All reflections on a Guinier photograph of **I** were indexed in a primitive cubic cell with a unit cell edge $a = 10.9532(5)$ Å. An indexing of the X-ray pattern of **II** was successful by doubling the unit cell edge. In this case, all reflections were indexed in a face-centered cubic cell with a unit cell edge $a = 22.179(1)$ Å.

For the structure determination of **I**, a suitable single crystal ($0.12 \times 0.12 \times 0.12$ mm^3) was glued with epoxy cement on a tip of a Pyrex fiber, and mounted on a goniometer head of a Nonius CAD4 diffractometer. Unit cell dimensions were refined on the base of 24 well-centered reflections. Data were collected (Table 1) at ambient temperature to a maximum 2θ of 55° using an $\omega-2\theta$ mode. After correction for polarization and Lorentz effects, a semiempirical absorption correction was applied to data based on azimuthal scans of 7

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(1) (a) von Schnering, H. G.; Menke, H. *Angew. Chem.* **1972**, *84*, 30. (b) Menke, H.; von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1973**, *395*, 223.

(2) A brief survey of cadmium and mercury pnicitehalides is given in: Rebbah, H.; Rebbah, A. *J. Solid State Chem.* **1994**, *113*, 1. For more recent results, see: Shevelkov, A. V.; Dikarev, E. V.; Popovkin, B. A. *J. Solid State Chem.* **1996**, *126*, 324 and references therein.

(3) Shevelkov, A. V. *Book of Abstracts*, VIth European Conference on Solid State Chemistry, Zürich, Sept. 17−20, 1997; ML7.

(4) *Handbuch der Präparativen Anorganischen Chemie*; Brauer, G., Ed.; Ferdinand Enke Verlag: Stuttgart, 1975; Chapter 12.

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Table 2. Atomic Coordinates[a] ($\times 10^4$) and Thermal Displacement Parameters[b] ($Å^2 \times 10^3$) for **I**

atom	site	x	y	z	*U*(eq)
I(1)	2a	0	0	0	12(1)
I(2)	6d	5000	0	2500	17(1)
Sn(1)	24k	0	3426(5)	1537(5)	14(1)
Sn(1′)	24k	0	3092(4)	1135(5)	14(1)
P(1)	16i	1921(1)	1921	1921	9(1)
P(2)	6c	2500	0	5000	10(2)

[a] Occupancies: 45(1)%, Sn(1); 55(1)%, Sn(1′); 54.8(3)%, P(2). [b] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Important Interatomic Distances (Å) and Angles (deg) in **I**

P(1)−P(1)	2.196(4)	I(1)−8P(1)	3.656(2)
−3Sn(1′)	2.610(1)	−12Sn(1′)	3.608(1)
−3Sn(1)	2.706(3)	−12Sn(1)	4.113(2)
P(2)−4Sn(1)	2.570(6)	I(2)−8P(1)	4.022(2)
Sn(1)−Sn(1′)	2.950(1)	−4P(2)	3.873(1)
−2P(1)	2.706(3)	−8Sn(1)	3.648(2)
Sn(1′)−Sn(1)	2.950(1)	−8Sn(1′)	3.662(1)
−2P(1)	2.706(1)	−4Sn(1)	3.927(1)
−P(2)	2.570(6)	−4Sn(2)	4.283(1)

P(1)−P(1)−P(1)	111.8(1)
Sn(1′)−P(1)−Sn(1′)	107.0(2)
P(1)−P(1)−Sn(1)	100.8(2)
Sn(1′)−P(1)−Sn(1)	117.2(1)
Sn(1′)−P(1)−Sn(1)	108.1(1)
Sn(1)−P(1)−Sn(1)	116.58(9)
Sn(1′)−P(2)−Sn(1′)	109.78(5)
Sn(1′)−P(2)−Sn(1′)	108.9(1)
P(2)−Sn(1′)−P(1)	102.0(2)
P(1)−Sn(1′)−P(1)	107.45(7)
P(2)−Sn(1′)−Sn(1)	118.45(8)
P(1)−Sn(1′)−Sn(1)	112.8(1)
P(1)−Sn(1)−P(1)	102.1(1)
P(1)−Sn(1)−Sn(1′)	94.5(1)

reflections. Systematic extinctions showed that two space groups, $P\bar{4}3n$ and $Pm\bar{3}n$, were the possibilities. The structure was successfully solved in a centric space group $Pm\bar{3}n$ by direct methods,[5a] which located positions of all atoms. Isotropic refinement showed that two atoms, Sn and P(2), had enormously high thermal displacement parameters. Inspection of a $\Delta\rho$ map revealed the split of the position of the Sn atom into two positions, Sn(1) and Sn(1′), lying 0.57 Å from each other. Two partially occupied tin atomic positions with the occupancy sum fixed as unity, as well as the occupancy factor for the P(2) atom were introduced into the anisotropic refinement,[5b] that led to the composition $Sn_{24}P_{19.29}I_8$. Refinement of the occupancy factors of the P(1) atom, and of both independent iodine atoms did not reveal any deviation of these factors from unity. Final atomic parameters and important bond lengths and angles are listed in Tables 2 and 3, respectively. Refinement in an acentric space group $P\bar{4}3n$, which is characteristic of $Ge_{38}P_8I_8$,[1a] gave less accurate results and did not remove the split of the tin atomic position.

^{119}Sn Mössbauer spectra were recorded at 300 K using a conventional spectrometer of the electrodynamic type operating in a constant acceleration mode, the drive being routinely calibrated with a metallic iron foil. The source ($Ca^{119m}SnO_3$) was kept at room temperature. All isomer shifts are referred to $CaSnO_3$.

Conductivity measurements were performed on a monophase powder sample using a standard high-frequency, contact-free Q-technique in the temperature range 120−335 K.

Results and Discussion

A view of the crystal structure of **I** is shown in Figure 1. The basic building unit of the structure is a 3D net comprised of tin and phosphorus atoms. The P(1) atoms are joined into pairs with a P−P separation of 2.20 Å, which is normal for the ordinary P−P bond.[6] Each P(1) atom is further bound to three tin atoms, thus completing its distorted tetrahedral coordination.

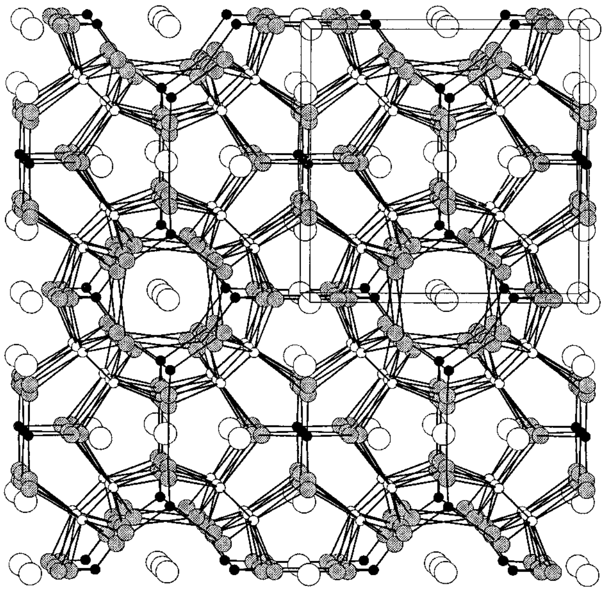

Figure 1. A view of the crystal structure of **I**. Large open circles, iodine; small open circles, P(2); black circles, P(1); shaded circles, tin.

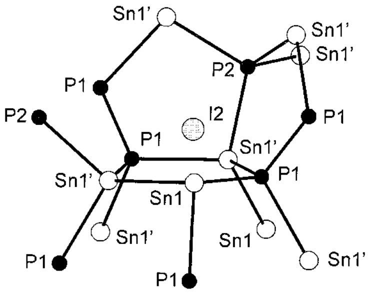

Figure 2. A fragment of the crystal structure of **I** showing coordination of the tin and phosphorus atoms in the ordered way.

The P(2) atom is surrounded by four tin atoms forming an almost regular tetrahedron. In all cases the Sn−P distances cover the range of 2.57−2.71 Å, which is comparable with the Sn−P distances of 2.66 Å found in SnP_3 and Sn_4P_3.[7] Coordination of two independent tin atoms is different. The Sn(1′) atom has a distorted tetrahedral coordination, 3P + 1Sn, while the Sn(1) atom has only three neighbors, 2P + 1Sn. The separation between the Sn(1) and P(2) atomic positions is too short (2.021 Å), therefore, there are no real Sn(1)−P(2) distances, and the coordination of Sn(1) is best described as having three neighbors and one lone electron pair. Then, the P(2) atom, which occupies partially the 6c atomic position, is present when Sn(1) is absent, and is absent when Sn(1) is present. The independently refined occupancy factors for the Sn(1) and P(2) atoms correlate well, their sum deviates from 100% by only 0.2, that is below the esd's. The Sn−Sn distance is 2.95 Å, that is only slightly longer than in Li_5NaSn_4 (2.93 Å).[8] Coordination of the tin and phosphorus atoms is shown in Figure 2.

Two independent iodine atoms are not involved in the 3D net. They occupy large holes of two different types, the closest iodine-to-neighbor distance being 3.61 Å. The I(1) atom is

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(5) (a) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: Oxford, 1985; p 175−189. (b) Sheldrick, G. M. In *Crystallographic Computing 6*; Flack, H. D., Parkanyi, L., Simon, K., Eds.; Oxford University Press: Oxford, 1993; p 111−122.

(6) von Schnering, H. G.; Hönle, W. *Chem. Rev.* **1988**, *88*, 243.

(7) (a) Gullman, J.; Olofsson, O. *J. Solid State Chem.* **1972**, *5*, 441. (b) Olofsson, O. *Acta Chem. Scand.* **1970**, *24*, 1153.

(8) Volk, K.; Müller, W. *Z. Naturforsch.* **1978**, *B33*, 393.

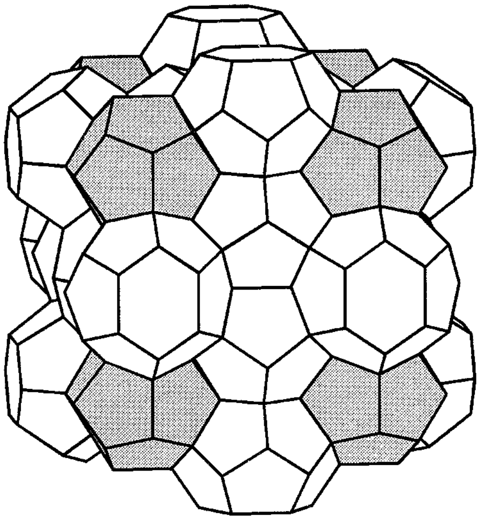

Figure 3. A polyhedral presentation of the crystal structure of **I**. Pentagonal dodecahedra around the I(1) atoms are drawn in gray, tetrakaidodecahedra around the I(2) atoms are drawn in white.

surrounded by 20 atoms (12Sn + 8P) forming a pentagonal dodecahedron, and the I(2) atom is surrounded by 24 atoms (12Sn + 12P) forming a tetrakaidodecahedron. Two types of polyhedra share faces; the polyhedral presentation of the structure of **I** is shown in Figure 3. Such a presentation makes it immediately evident that the structure of **I** belongs to the clathrate-I type.

Literature data show that alkali metal stannides[9] M_8Sn_{46} belong to the same structure type. In these compounds, the anionic 3D net is composed of 46 tin atoms per unit cell, the Sn−Sn distance being 2.66−2.73 Å, while alkali metal atoms occupy the large holes. There exist examples of defect structures of the same type,[10] e.g., in the structure of Rb_8Sn_{44}, which crystallizes in a space group $Pm\bar{3}n$, the *6c* positions of Sn atoms are partially occupied. The vacancies in the Group 14 element sublattice are necessary to fulfill the Zintl−Klemm concept. If all 46 tin atoms were four-bonded (4b),[11] the (Sn_{46}) net would be electron-precise without alkali-metal atoms. Each vacancy generates four 3b tin atoms, which are necessary for transferring electrons from the A cations, and with exactly two vacancies, the stannides K_8Sn_{44} and Rb_8Sn_{44} are narrow gap semiconductors.[12] Recent studies, including structure refinements, conductivity measurements and band structure calculations, confirm the necessity of the vacancies in the 6c position,[12] the very existence of fully occupied A_8E_{46} phases (E = Si, Ge, Sn) being doubtful. The same 6c position in the structure of **I** is 54.8% occupied by the P(2) atoms; thus, there are (on average) only 43.29 atoms per unit cell in the respective 3D net. As in the case of the A_8Sn_{44} phases, the vacancy free structure would violate greatly the Zintl−Klemm concept. With all tin and phosphorus atoms being four-bonded in a vacancy free structure, there would be 22 extra electrons per $(Sn_{24}P_{22})$ net or, accounting for eight iodine atoms, 14 extra electrons per $(Sn_{24}P_{22}I_8)$ formula. Each vacancy at the P(2) site removes five electrons, thus, there should be 14/5 = 2.8 vacancies to fulfill the Zintl−Klemm concept. The corresponding composition of the phase would be $Sn_{24}P_{19.2}I_8$, which is very close to the composition $Sn_{24}P_{19.29\pm0.2}I_8$ determined from the structure refinement. The conductivity measurements show the semiconductor-like temperature dependence ($E_g \approx 0.04$ eV), which indicates that **I** obeys the Zintl−Klemm concept.

The vacancies cause the split of the tin atomic positions into two, the 4b Sn(1′) and 3b Sn(1) positions. The former surrounds the present P(2) atoms, while the latter surrounds the vacancies and is characterized by three bonds and one lone electron pair. The ^{119}Sn Mössbauer spectroscopy confirms the difference in the nature of the two positions. The spectrum recorded from the monophase sample of **I** is a superposition of two components with the parameters $\delta = 1.50 \pm 0.02$, $\Delta = 0.12 \pm 0.02$ mm s^{-1}, and $\delta = 2.55 \pm 0.02$, $\Delta = 0.44 \pm 0.02$ mm s^{-1}, respectively. The chemical isomer shift of the first component is just a little bit lower than reported for Na_5SnP_3 (1.54 mm s^{-1}),[13] where tin is tetrahedrally coordinated by phosphorus, and thus, the first component can be assigned to the Sn(1′) atom. The value of the quadrupole splitting in Na_5SnP_3 (0.59 mm s^{-1}) is higher than in our spectrum, which presumably reflects the chemical difference in the coordination of tin, 4P in Na_5SnP_3, and 3P + 1Sn for the Sn(1′) atom in **I**, for the less electronegative and less symmetric environment about the Sn(1′) atom results in less withdrawal of electron density. Both chemical isomer shift and quadrupole splitting of the second component are the same as in Sn_4P_3,[14] where coordination of two crystallographically independent tin atoms is described as having three phosphorus neighbors and a stereoactive lone electron pair, which spreads toward three more distant (3.24 Å) Sn/P atoms.[15] This component can be assigned to the Sn(1) atom, the coordination of which (2P + 1Sn) is also completed by three distant tin atoms (3.25−3.34 Å). Since both tin atoms, Sn(1) and Sn(1′), can be described as being sp^3 hybridized, the larger quadrupole splitting of the second component is consistent with the significant p character of the lone electron pair of Sn(1), and the consequent deshielding of the 5s orbital results in the more positive chemical isomer shift of the second component.

The crystal structure of **II** is still unknown. However, the unit cell dimensions, $a = 22.179(1)$ Å, may indicate that it has the same structural motif; and the ordering of tin atoms within the unit cell, which is 8 times larger than for **I**, could be the reason for the unit cell enlargement. Also, the exact composition of **II**, in particular the arsenic content, cannot be determined very precisely. On the base of the synthetic conditions and the accuracy of the X-ray powder diffraction determination we can formulate the composition of **II** as $Sn_{24}As_{19.3\pm0.2}I_8$. Our attempts to synthesize the antimony analogue of **I** and **II** have not led to the preparation of any ternary phase in the Sn−Sb−I system.

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Supporting Information Available: One X-ray crystallographic file, in CIF format, is available free of charge via the Internet at http://pubs.acs.org.

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[9] (a) Gallmeier, J.; Schäfer, H.; Weiss, A. *Z. Naturforsch.* **1969**, *24*, 665. (b) Grin', Y. N.; Melekhov, L. Z.; Chutonov, K. A.; Yatsenko, S. P. *Kristallografiya* **1987**, *32*, 497.

[10] (a) Cross, C.; Pouchard, M.; Hagenmuller, P.; Kasper, J. S. *Bull. Soc. Chim. France* **1968**, *1968*, 2737. (b) von Schnering, H. G.; Nesper, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1059 and references therein.

[11] von Schnering, H. G. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 33.

[12] (a) Zhao, J.-T.; Corbett, J. D. *Inorg. Chem.* **1994**, *33*, 5721. (b) Baitinger, M.; Grin, Yu.; von Schnering, H. G. *Book of Abstracts*, VIth European Conference on Solid State Chemistry, Zürich, Sept. 17−20, 1997; PA116. (c) Miller, G. M. In *Chemistry, Structure, and Bonding of Zintl Phases and Ions*; Kauzlarich, S. M., Ed.; VCH Publishers: New York, 1996; p 23−25.

[13] Asbrand, M.; Berry, F. J.; Eisenmann, B.; Kniep, R.; Smart, L. E.; Thied, R. C. *J. Solid State Chem.* **1995**, *118*, 397.

[14] Presniakov, I. A.; Shatruk, M. M.; Shevelkov, A. V. In preparation.

[15] Eckerlin, P.; Kischio, W. *Z. Anorg. Allg. Chem.* **1968**, *363*, 1.