Full Articles

Synthesis and the crystal and electronic structure of Hg_4AsI_5

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New mercury arsenide iodide Hg_4AsI_5 was synthesized and its crystal and electronic structure was determined. The crystal structure is layered. The layers are composed of alternating $AsHg_4$ tetrahedra and IHg_8 Archimedean antiprisms and are bound by the iodine atoms, which form short Hg—I bonds with all mercury atoms. Band structure calculations provided evidence for very weak interactions between the iodine atoms of the adjacent layers and the ionic character of the iodine atom centering the Archimedean antiprism. Hence, individual $[AsHg_4I_4]^+$ clusters and I^- anions can be distinguished.

Key words: mercury, pnictide halides, crystal and electronic structure.

Pnictide halides of Group 12 elements belong to a large family of compounds crystallizing in various structural types due to the ability of pnictogens (Pn, Group 15 elements) to form anions of different complexity, from monoatomic Pn^{3-} to one-dimensional infinite $_{\infty}{}^1(Pn^{1-})$.[1] The structure of the pnictogen fragment is directly related to the formal oxidation state of the pnictogen atoms, which, in turn, is associated with the stoichiometry and structure of the compounds in question. Because of this, phases containing the same anion of a Group 15 element often have identical composition and similar structures. For example, pnictide halides of Group 12 elements containing only separate Pn^{3-} anions can be divided into two structural groups. One group includes compounds of 3 : 1 : 3 stoichiometry, which have defect structures of sphalerite or wurtzite[2—4] (for example, Zn_3PI_3) or their complex derived types[5] (for example, Cd_3PCl_3). Compounds belonging to another group are structural analogs of the well-known salts of Millon's base[6,7] and have supramolecular structures (for example, $[Hg_2P]_2(HgBr_4)$).

In the present study, we synthesized new mercury pnictide halide Hg_4AsI_5 and established its crystal and electronic structure. This compound contains the monoatomic As^{3-} anion and forms its own crystal structure type.

Results and Discussion

New mercury arsenide iodide Hg_4AsI_5 was synthesized by the ampoule technique at 693 K starting from mercury, mercury(II) iodide, and gray arsenic. The result-

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ing red Hg_4AsI_5 compound is stable to atmospheric moisture and exists as plate crystals, which easily flake off. An increase in the synthesis temperature in an evacuated ampoule to 773 K led to the formation of a mixture of mercury and arsenic iodides instead of the target phase. In this case, the $Hg_4As_2I_3$ compound, which has been found earlier[8] in the Hg—As—I system, was not produced.

The crystal structure of the new mercury arsenide iodide was established by X-ray diffraction. The crystal structure was solved and refined in the space group *Cmca*, which gave the formula Hg_4AsI_5. The composition of this compound was additionally confirmed by energy-dispersive X-ray spectroscopy (EDX) analysis. The ratio obtained from the EDX data (Hg : As : I, 34.8(2) : 11.0(1) : 54.2(2)) is in satisfactory agreement with the ratio calculated for the formula Hg_4AsI_5 (Hg : As : I, 40 : 10 : 50) taking into account the systematic error of energy-dispersive X-ray spectroscopy.

The crystal structure of Hg_4AsI_5 is characterized by the presence of eight crystallographically independent atomic sites. The only crystallographically independent arsenic atom is in a tetrahedral environment formed by four mercury atoms (Fig. 1, *a*), which are located at distances of 2.49—2.50 Å (Table 1). These distances are typical of Hg—As bonds.[9,10] Three crystallographically independent mercury atoms have a similar, almost linear, coordination environment formed by one arsenic atom and one iodine atom. The distance between the mercury and iodine atoms is 2.63 Å. Such short Hg—I bond lengths have not been found in mercury pnictide iodides. However, these distances are virtually equal to the Hg—I distance in the yellow modification of HgI_2.[11] Three iodine atoms, *viz.*, I(1), I(2), and I(3), are terminal, each being bound to only one mercury atom. The coordination of the I(4) atom is unusual. This atom is surrounded by eight mercury atoms at distances of 3.54—3.58 Å, and these atoms form a slightly distorted Archimedean antiprism (see Fig. 1, *b*).

The overall view of the crystal structure of Hg_4AsI_5 is shown in Fig. 2. The layers are formed by the polyhedra

Table 1. Interatomic distances and bond angles in the Hg_4AsI_5 structure

Distance	*d*/Å	Angle	ω/deg
Hg(1)—I(2)	2.627(1)	As—Hg(1)—I(2)	175.70(6)
Hg(2)—I(3)	2.630(1)	As—Hg(2)—I(3)	175.43(7)
Hg(3)—I(1)	2.628(1)	As—Hg(3)—I(1)	173.70(5)
As—Hg(1)	2.494(2)	Hg(1)—As—Hg(2)	103.02(8)
As—Hg(2)	2.489(2)	Hg(1)—As—Hg(3)	112.91(5)
As—Hg(3)*	2.497(1)	Hg(2)—As—Hg(3)	112.97(5)
I(4)—Hg(1)*	3.5358(7)	Hg(3)—As—Hg(3)	102.44(8)
I(4)—Hg(2)*	3.5404(7)		
I(4)—Hg(3)*	3.531(1)		
I(4)—Hg(3)*	3.584(1)		
I(2)...I(1)*	3.986(1)		
I(3)...I(3)	3.661(2)		

* There are two identical bonds in the structure.

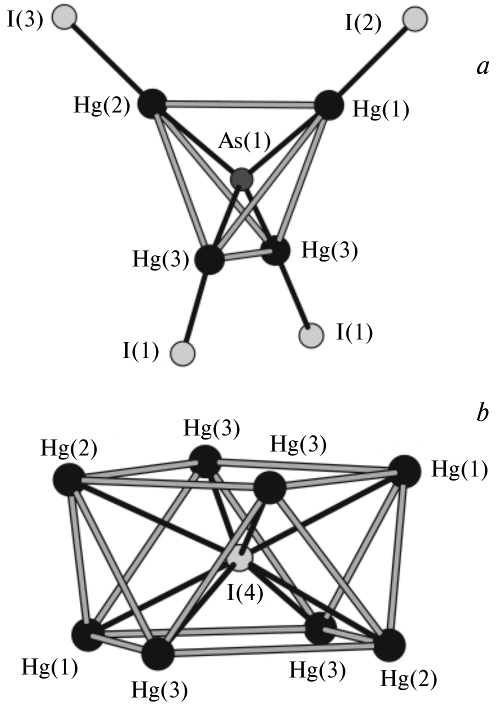

Fig. 1. Coordination environment of the As (*a*) and I(4) (*b*) atoms in the Hg_4AsI_5 structure.

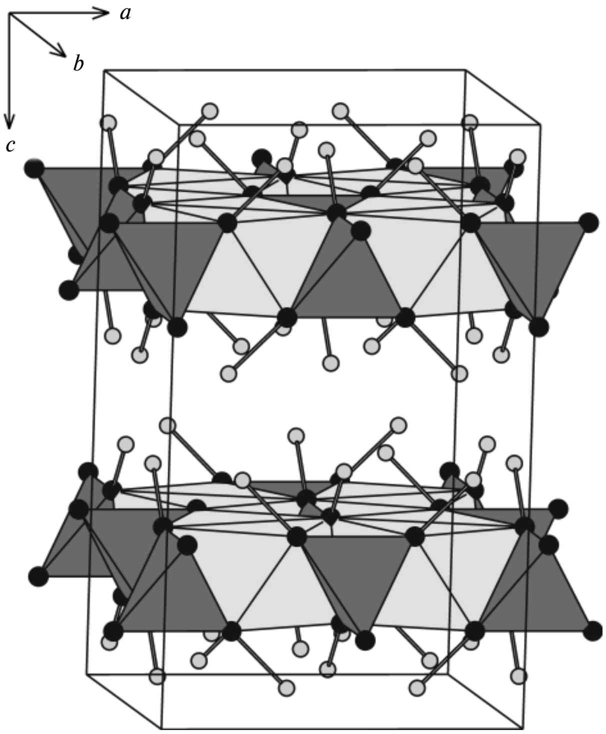

Fig. 2. Overall view of the crystal structure of Hg_4AsI_5.

centered with the As^{3-} and $I(4)^-$ anions.[12] The layers consist of the edge-sharing $AsHg_4$ tetrahedra and IHg_8 Archimedean antiprisms alternating in a 1 : 1 ratio and are bound by the terminal iodine atoms. The layers alternate along the *c* axis and are linked to each other through weak interactions between the terminal iodine atoms. The I...I distances are in the range of 3.66—4.10 Å. A comparison with the van der Waals radius of iodine (2.0 Å)[13] showed that the shortest I(3)...I(3) distance (3.66 Å) is substantially smaller than twice the radius of iodine and provided evidence for a certain interaction between the layers.

Analysis of the coordination of the atoms involved in the crystal structure of Hg_4AsI_5 unambiguously revealed their oxidation states. In the absence of homonuclear bonds, the oxidation state −3 should be assigned to the tetrahedrally coordinated arsenic atom. The linearly coordinated mercury atoms, which are not involved in Hg—Hg bonds, have an oxidation state +2. The iodine atoms have an oxidation state −1 regardless of their coordination. Consequently, the new compound can be described as $(Hg^{+2})_4(As^{-3})(I^{-1})_5$. Band structure calculations for Hg_4AsI_5 in the density functional approximation demonstrated that the above-given description is formal and merely indicates that all atoms involved in the structure reach an electron octet. It can be seen from the density of state plots (Fig. 3) that the *d* orbitals of the mercury atoms make a noticeable contribution to the formation of the Hg—I bonds and, particularly, the Hg—As bonds. In addition, the contribution of the orbitals of the terminal iodine atoms to the electronic states near the Fermi level substantially differs from the contribution of the orbitals of the I(4) atom. Further analysis of the orbital contributions revealed the presence of nonnegligible interactions between the mercury atoms and the I(4) atom and the absence of interactions between the iodine atoms of the adjacent layers. Finally, the charge on the I(4) atom (−0.5) is substantially higher in absolute value than the charges on the other iodine atoms. Consequently, the crystal structure of Hg_4AsI_5 contains the covalently bonded $[AsHg_4I_4]^+$ fragments (clusters) (see Fig. 1, *a*) alternating with I^- ions, and the compound can be described by the formula $[AsHg_4I_4]I$.

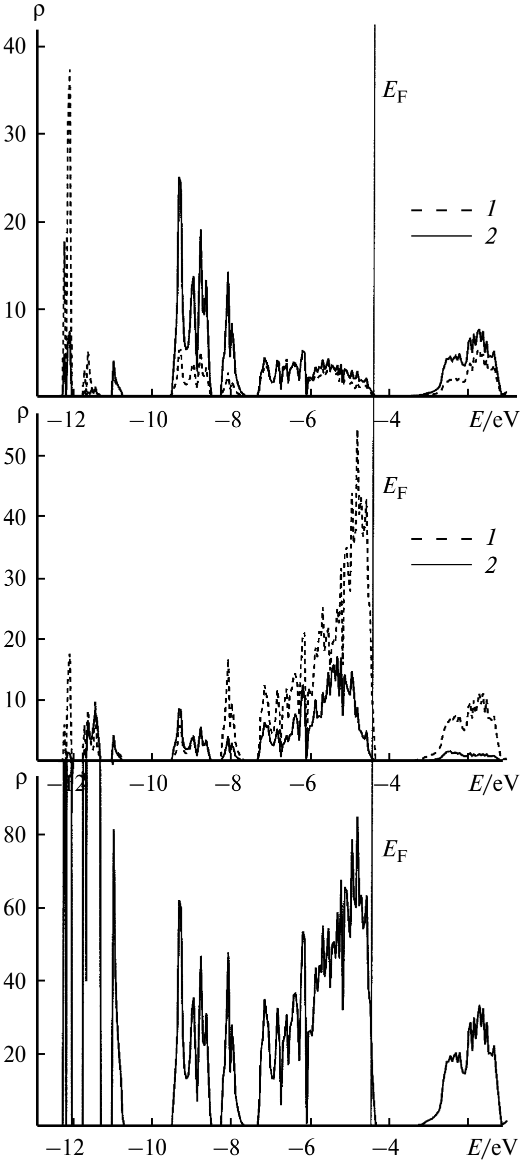

Fig. 3. Density of states (ρ) calculated for the Hg_4AsI_5 structure: *a*, *1*, As (s+p); *2*, Hg (s+p); *b*, *1*, I(1) + I(2) + I(3); *2*, I(4); *c*, total density.

To summarize, the new mercury arsenide iodide Hg_4AsI_5 has a layered structure of the previously unknown type. In this structure, the layers consist of alternating positively charged $[AsHg_4I_4]^+$ clusters and I^- ions, which have an antiprismatic coordination. Interactions between the iodine atoms of the adjacent layers are very weak, which is responsible for the specific mechanical properties of this compound.

Experimental

The Hg_4AsI_5 compound was synthesized according to the standard ampoule technique. Gray arsenic (special purity grade), mercury (chemical purity grade), and mercury(II) iodide (chemical purity grade) were used as the starting reagents. The $2As : 3Hg : 5HgI_2$ mixture was placed into a quartz ampoule (inner diameter was 8 mm), which was evacuated to the residual pressure of $2 \cdot 10^{-2}$ Torr and then sealed. Annealing was performed at 693 K for five days followed by cooling in a switched-off oven. The resulting compound was obtained as a red polycrystalline clinker, which slightly darkened in air.

Powder X-ray diffraction analysis of the annealing products was carried out on a STADI-P (STOE) powder diffractometer (Cu-Kα1 radiation). A comparison of the X-ray diffraction pattern with the pattern calculated from the single-crystal X-ray diffraction data demonstrated that the sample contained a new phase with a small (<10%) impurity of the starting compounds.

Table 2. Details of X-ray data collection and refinement of the crystal structure of Hg_4AsI_5

Parameter	Characteristics
Molecular formula	Hg_4AsI_5
Molecular weight	1511.78
Crystal system	Orthorhombic
Space group	*Cmca*
a/Å	11.927(1)
b/Å	12.128(1)
c/Å	19.766(3)
V/Å^3	2859.0(8)
Z	8
d_{calc}/g cm^{-3}	7.025
μ/mm^{-1}	55.87
Scan range	$2.61 < \theta < 28.31$
Number of measured reflections	11163
Number of independent reflections	1794
Number of parameters in refinement	54
R_1 $(I \geq 2\sigma(I))$*	0.0597
wR_2** (based on all reflections)	0.1615
Goodness-of-fit on F^2	1.066

* $R_1 = \Sigma||F_0| - |Fc||/\Sigma|F_0|$.

** $wR_2 = \{\Sigma[w(F_0{}^2 - F_c{}^2)^2]/\Sigma[w(F_0{}^2)^2]\}^{1/2}$, $w = \{\sigma^2(F_0)^2 + 0.0082[(F_0{}^2 + 2F_c{}^2)/3]^2 + 38.1839[(F_0{}^2 + 2F_c{}^2)/3]\}^{-1}$.

The X-ray diffraction data were collected from a red plate single crystal of Hg_4AsI_5 of dimensions 0.10×0.09×0.06 mm^3, which was taken from the annealing products, on a Bruker SMART APEX diffractometer equipped with a CCD detector (Mo-Kα radiation, ω scanning technique with a step of 0.3° and exposure time of 20 s frame^{-1}) at 173 K (Bruker KRYO-FLEX). The principal crystallographic data and structure refinement parameters are given in Table 2. The X-ray data were processed with the use of the Bruker SAINT program package.[14] The frames were integrated in the orthorhombic unit cell, and 11163 reflections with the maximum angle $2\theta = 56.62°$ were obtained, of which 1794 reflections were independent. The empirical absorption correction was applied using the SADABS program[15] ($R_{int} = 0.0689$). The structure was solved and refined by the full-matrix least-squares method against F^2 in the space group *Cmca* (No. 64) with the use of the SHELX-97 program package.[16,17] The final anisotropic refinement converged to $R_1 = 0.0597$.*

Energy-dispersive X-ray spectroscopy (EDX) analysis was performed on a JEOL JSM-5510 scanning electron microscope (accelerating voltage was 20 kV) equipped with an INCA analytical facility (Oxford Instruments) using Hg_4AsI_5 crystals, which were placed in the sample holder of the microscope.

The band structure of Hg_4AsI_5 was calculated in the density functional approximation by the linear muffin tin orbital method in the atomic sphere approximation with the use of the TB-LMTO-47 program package.[18] Prior to the calculations of the total and projected densities of states, the convergence of self-consistent calculations for 96 k points in the irreducible Brillouin zone was achieved.

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* Additional details of the crystal structure study (deposition number CSD-416238) can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, fax: +(49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de.