Synthesis, Crystal and Electronic Structure of $[Hg_7As_4](AgI_3)_2$, a Novel Supramolecular Complex with the Off-Plane AgI_3^{2-} Guest Anion

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A novel supramolecular inorganic complex $[Hg_7As_4](AgI_3)_2$ has been prepared and its crystal structure determined. It crystallizes in the cubic system (space group $Pa\bar{3}$) with the unit cell parameter a = 13.138(1) Å and Z = 4. The crystal structure comprises a three-dimensional positively charged host framework $[Hg_7As_4]^{4+}$ with AgI_3^{2-} guest anions trapped in each cavity of the framework. The guest anion shows an unusual off-plane geometry (C_{3v} symmetry), with a large, anisotropic thermal displacement parameter for the silver atom, which lowers significantly upon cooling from 293 down to 120 K. A study of the electronic structure shows that, although the host-guest interaction is weak and diffuse, it governs both the geometry of the guest anion and its positioning within the framework cavities.

Introduction

Supramolecular architectures with three-dimensional (3D) host frameworks possess a huge variety of crystal structures. A number of supramolecular complexes in which the positively charged 3D host substructures are built from linear mercury and tetrahedral pnicogen atoms have been reported over the past few years.[1−4] The combination of linear and tetrahedral units in the host substructure, together with the possibility of forming homonuclear bonds, provides a rich structural diversity of such complexes. Indeed, the crystal chemistry of the compounds under consideration ranges from phosphorus and arsenic analogues of the Millon phases[1] to a group of symmetric complexes with $[Hg_6Z_4]^{4+}$ host frameworks.[2] The positive charge of the host framework in these compounds is compensated by the halometallate anions of different shape and size that reside in the host framework cavities. Due to large separations between the host and guest moieties their interactions are limited to weak electrostatic forces.

It is well known that the guest moieties usually serve as templates during the formation of supramolecular complexes.[5] Host frameworks, in turn, may influence the geometry of the guests. Hence, the formation of a supramolecular architecture is often achieved by a mutual adjustment of the host and guest substructures. Examples of such an adjustment were shown in our previous work where we reported a family of new supramolecular complexes[4] in which the SnX_3^- (X = Cl, Br, I) guests are encapsulated in the cavities of the Hg−Z (Z = P, As, Sb) host framework. Evidently, the formation of a supramolecular complex is facilitated by a certain "crystallographic flexibility" of the guest, or, in general, by the possibility that the atoms of the guest moiety have different coordination (and oxidation) numbers. For silver, for example, the generic formula of the halometallate anions can be written as $AgX_n^{(n-1)-}$ ($2 \leq n \leq 4$; X = Cl, Br, I). Examining the possibility of the formation of supramolecular assemblies with $AgX_n^{(n-1)-}$ guest anions, we unexpectedly discovered a novel complex $[Hg_7As_4](AgI_3)_2$ in which an unusual off-plane AgI_3^{2-}anion resides in the cavities of a Hg−As cationic framework.

Here we report on the synthesis and crystal structure of $[Hg_7As_4](AgI_3)_2$. The host-guest interactions in the title compound, which lead to the observed off-plane geometry of the guest AgI_3^{2-} anion, are also discussed on the basis of the ab initio molecular structure and extended Hückel band-structure calculations.

Results

$[Hg_7As_4](AgI_3)_2$ was prepared from a stoichiometric mixture of mercury(II) iodide, arsenic, silver powder, and liquid mercury by a two-step ampoule synthesis (see Exp. Sect. for details). The sample formed as a dark-brown polycrystalline powder. The compound is air- and moisture-stable, and it melts incongruently at 675 K.

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For the structure investigation a suitable single crystal was selected from a sample prepared from a nonstoichiometric mixture of starting reagents as described in the Exp. Sect. The crystal structure of the new compound was determined by single-crystal X-ray diffraction methods at ambient temperature (Table 3). Analysis of the systematic absences in the data set revealed one possible space group $Pa\bar{3}$ (no. 205). The positions of the mercury, iodine, arsenic, and silver atoms were localized by direct methods (SHELXS 97[6]). It should be noted that the electron-density peak assigned to the silver atom position was the lowest one. Refinement of the crystal structure (SHELXL 97[6]) showed that the silver atom has a large thermal displacement parameter. Nevertheless, the refinement of the occupancy of the silver atom position confirmed this position to be fully occupied. Final anisotropic refinement led to quite acceptable R values ($R1$ = 3.9% $wR2$ = 8.4%). However, it also revealed that the silver atom has a strongly prolate thermal ellipsoid, which could possibly indicate that the silver position is split. In order to check if this was the case, a low-temperature (120 K) X-ray structure investigation was carried out. The analysis of the diffraction frames showed the absence of superstructural reflections and confirmed the space group to be the same as that determined during the ambient-temperature diffraction experiment. The crystal structure was successfully refined ($R1$ = 4.2%, $wR2$ = 9.1%) with the atomic positions determined in the room-temperature experiment (Table 1). The thermal displacement parameters of all atoms, and especially of the silver atom (Table 1), lowered significantly. No electron-density peaks were observed near the position of the silver atom, which could be assigned to the split position of the silver.

Table 1. Atomic positions for $[Hg_7As_4](AgI_3)_2$ at 293 K and equivalent displacement parameters for the compound at 293 and 120 K

Atom	Wykoff	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq} [Å^2][a]	
					293 K	120 K
Hg(1)	24d	0.2122(1)	0.4165(1)	0.4521(1)	0.0341(3)	0.0159(2)
Hg(2)	4b	1/2	1/2	1/2	0.0399(5)	0.0174(5)
I	24d	0.1659(1)	0.5524(1)	0.2453(1)	0.0270(3)	0.0121(3)
As(1)	8c	0.0528(1)	0.0528(1)	0.0528(1)	0.0132(6)	0.0054(7)
As(2)	8c	0.3903(1)	0.3903(1)	0.3903(1)	0.0143(7)	0.0079(8)
Ag	8c	0.2705(3)	0.2705(3)	0.2705(3)	0.101(1)	0.043(1)

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

Table 2. Selected interatomic distances and bond angles for $[Hg_7As_4](AgI_3)_2$ at 293 K

Distances [Å]	
As(1)−As(1)	2.405(6)
As(1)−Hg(1)	2.510(1) ×3
As(2)−Hg(1)	2.500(1) ×3
As(2)−Hg(2)	2.497(3)
Ag−I	2.711(1) ×3
Hg(1)−I	3.307(1)
Hg(1)−I	3.446(1)
Hg(1)−I	3.573(1)
Hg(1)−I	3.575(1)
Angles [°]	
Hg(1)−As(1)−Hg(1)	113.00(6) ×3
As(1)−As(1)−Hg(1)	105.66(7) ×3
Hg(2)−As(2)−Hg(1)	105.84(7) ×3
Hg(1)−As(2)−Hg(1)	112.85(6) ×3
As(2)−Hg(1)−As(1)	166.94(9)
As(2)−Hg(2)−As(2)	180.00(6)
I−Ag−I	117.53(7) ×3

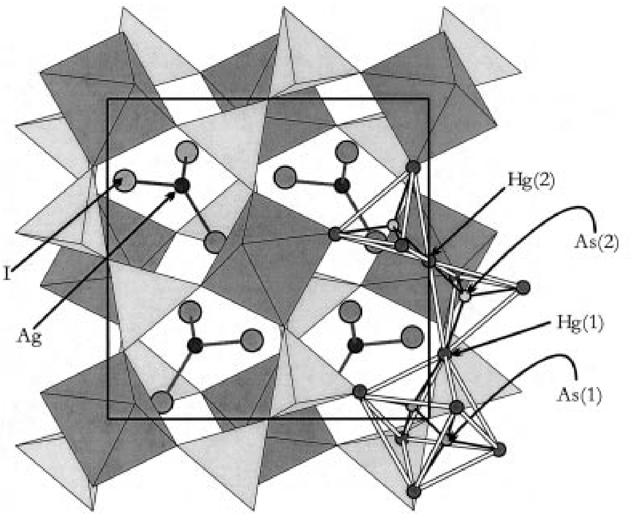

Figure 1. A view of the crystal structure of $[Hg_7As_4](AgI_3)_2$

Atomic parameters and selected interatomic distances and bond angles for $[Hg_7As_4](AgI_3)_2$ are listed in Tables 1 and 2, respectively. The crystal structure of the title compound (Figure 1) is composed of a positively charged $[Hg_7As_4]^{4+}$ host framework and AgI_3^{2-} guest anions encapsulated in the closed cavities of the host. The guest and host moieties are not connected by covalent bonds [d_{min}(Hg−I) = 3.31 Å], which is typical for supramolecular assemblies.

The host framework (Figure 1) is built from nearly linear-coordinated mercury and tetrahedrally coordinated arsenic atoms. There are two positions of the mercury atoms, Hg(1) and Hg(2), each of which is surrounded by two arsenic atoms. The additional neighbors of the Hg(2) atom lie 3.95 Å apart from it, and the As−Hg(2)−As angle appears to be 180°. In contrast with that, four iodine atoms of the guest anion serve as distant neighbors for the Hg(1) atom, the Hg−I separations being 3.31−3.56 Å. Thus, four iodine atoms of the guest complete the coordination sphere of the Hg(1) atom as a distorted octahedron, and, as a result, the As−Hg(1)−As angle (166.9°) departs from the ideal linear value.

The nearest neighbors of two crystallographically independent arsenic atoms are different (Figure 1). The As(1) atoms are joined into As_2^{4-} dumbbells and each As(1) atom is connected to one arsenic and three Hg(1) atoms. Six Hg(1) atoms surround the As(1)−As(1) dumbbell forming an $Hg(1)_6As(1)_2$ octahedral building block. The As(2) atom has a tetrahedral arrangement of three Hg(1) and one Hg(2) atom. Two $As(2)Hg(1)_3Hg(2)$ tetrahedra share a common Hg(2) vertex forming an Hg_7As_2 bitetrahedral group. The Hg_7As_2 and Hg_6As_2 building blocks all share the Hg(1) vertices to form a 3D $[Hg_7As_4]^{4+}$ host framework. The As−As (2.41 Å) and As−Hg (2.50−2.51 Å) distances within the framework are in good agreement with the values found in the literature for numerous mercury pnictide halides.[1−4]

The $[Hg_7As_4]^{4+}$ host framework has eight cavities of equal size per unit cell. To compensate for the positive charge of the host, the AgI_3^{2-} guest anions occupy each cavity. The guest anion departs significantly from the expected configuration, which would be a regular triangle with an in-plane silver atom (D_{3h} symmetry). All the Ag−I separations in the anion are the same (2.71 Å), while the I−Ag−I angle (117.5°) indicates that the silver atom does not reside in the plane of three iodine atoms. It lies 0.41 Å apart from the ligand plane, therefore the actual symmetry of the guest anion is C_{3v}.

The equilibrium geometry of the AgI_3^{2-} anion was calculated at different levels of theory (RHF and DFT). All calculations exploiting different basis sets and correlation potentials resulted in the expected planar triangle geometry (D_{3h} symmetry), with the Ag−I distances ranging from 2.93 to 3.01 Å depending on the type of calculation. Then, the positions of the three iodine atoms were frozen according to their positions in the crystal structure, while the position of the silver atom was optimized. Such calculations at the RHF level with the MP2 correction resulted in the C_{3v} geometry of the anion with an off-plane shift of the silver atom of 0.36 Å and three equidistant Ag−I contacts of 2.69 Å.

The band-structure calculations (at the EH level, Figure 2) showed that the bands below the Fermi level are composed of p-orbitals of I and As, s-orbitals of Hg, and d-orbitals of Ag. Analysis of the overlap population revealed the existence of strong covalent Hg−As and As−As bonding within the host framework and Ag−I bonding in the guest anion, whereas the host-guest Hg−I interaction is weak. A detailed analysis of the molecular orbitals of the AgI_3^{2-} anion revealed two sets of MOs corresponding to the Ag−I interaction, d(Ag)−p(I) bonding (between −14.5 and −12.3 eV) and d(Ag)−p(I) antibonding (between −12.3 eV and E_F). Both sets contain σ- and π-orbitals whose energies are only slightly sensitive to the small deviation of the anion geometry from D_{3h} towards C_{3v} symmetry.

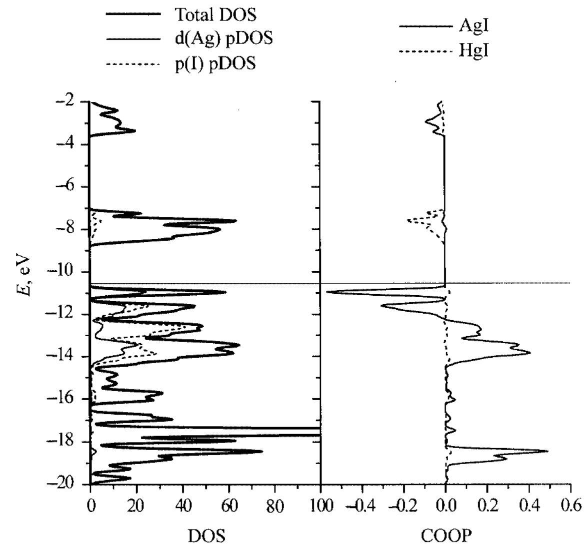

Figure 2. The Density of States (DOS) and Crystal Orbital Overlap Population (COOP) plots for $[Hg_7As_4](AgI_3)_2$

Discussion

The structure of the host framework of the title complex is similar to the structure of the hosts found in two earlier reported supramolecular architectures $[Hg_7As_4I_3]SnI_3$ and $[Hg_7P_4Br_3]SnBr_3$.[4] The main building blocks of the host frameworks of these two complexes are Hg_6Z_2 octahedra and Hg_7Z_2 bitetrahedal groups, their connection being the same as in the title compound. The main difference is that in the tin-containing complexes additional halogen atoms lie quite close to the mercury atoms thus modifying the host frameworks. The formulae of such frameworks can be written as $[Hg_7As_4I_3]^+$ and $[Hg_7P_4Br_3]^+$, respectively. They have two cavities of different size per formula unit and one guest anion − SnI_3^- or $SnBr_3^-$ − per formula unit is enough to compensate for the positive charge of the host framework These guest anions reside only in the larger cavities of the framework. In $[Hg_7As_4](AgI_3)_2$ the formal charge of the framework is +4, and all cavities in it have the same size. The electroneutrality of the complex is achieved by encapsulating the AgI_3^{2-} in each cavity of the host.

As was already mentioned, the geometry of the AgI_3^{2-} anion deviates considerably from the expected D_{3h} triangle. It is reasonable to compare the observed configuration of the guest anion with the geometry of AgX_3^{2-} (X = Cl, Br, I) anions in the literature. Analysis of the literature data surprisingly shows that there are only a small number of structurally characterized complexes that contain AgX_3^{2-}anions. The $AgCl_3^{2-}$ and $AgBr_3^{2-}$ anions have been isolated as their (dibenzo-18-crown-6)potassium and -rubidium salts.[7] In these two compounds the AgX_3^{2-} anions are regular (D_{3h} symmetry).

To the best of our knowledge there is only one known complex − $[PPh_3Me]_2[AgI_3]$[8] − that contains discrete AgI_3^{2-} anions. The triangular AgI_3^{2-} anion in it is reported to be only slightly distorted. The distance between the Ag atom and the ligand plane is only 0.04 Å. However, all three Ag−I distances in it are not equal and lie in the range 2.74−2.76 Å, thus lowering the symmetry of the anion from D_{3h} to effectively C_s.

The silver atom in the guest anion has a large thermal vibration amplitude in the direction perpendicular to the ligand plane. This indicate that the compound might undergo phase transformation (decomposition) at a relatively low temperature, or that the silver atom is distributed over two close crystallographic positions. However, neither the first nor the second supposition was proved to be the case.

The complex under investigation is stable up to 675 K, and the low-temperature X-ray diffraction experiment, as mentioned previously, unambiguously confirmed that the position of the silver atom is not split.

The off-plane construction of the AgI_3^{2-} guest anion, as well as the large thermal displacement parameter of the silver atom, deserve more discussion. It is clear from the results of the electronic structure calculations that the interaction of the host framework and guest anions is not strong and is predominantly of an electrostatic nature. Although the orbitals of As, Hg, Ag, and I apparently mix in the region below the Fermi level (from −10.8 to −14.5 eV), the overlap population analysis indicates that the Hg−I orbital interaction, which is responsible for the host-guest bonding, is weak and diffuse (Figure 2). On the contrary, bonding within the host and guest moieties is strongly covalent, and, consequently, the title compound can be formulated as pseudo-ionic: $[Hg_7As_4^{4+}](AgI_3^{2-})_2$. Each AgI_3^{2-} guest anion experiences the influence of 12 positively charged Hg(1) atoms of the host framework through distant Hg−I contacts (Figure 3). The Hg−I separations lying in the range of 3.31−3.58 Å are typical for a "secondary" Hg−I interaction. Analysis of the literature data[9] shows that the Hg−I separations in the 2+4 pseudo-octahedral array of mercury fall into two ranges: 2.62−2.64 Å for two collinear covalent Hg−I bonds, and 3.37−3.51 Å for four distant contacts. It is plausible to conclude that the positions of the iodine atoms in the title complex are governed by the arrangement of the positively charged mercury atoms of the rigid covalent framework. This leaves a limited space for the silver atom, forcing the latter to move from the ideal position at the center of the iodine triangle along its threefold axis. It should be noted that the observed 0.41 Å off-plane shift of Ag and the Ag−I distances of 2.72 Å are in very good agreement with the values calculated using a model with frozen iodine positions. Thus, the increase of the host anion energy due to the off-plane displacement of Ag is compensated for by the decrease of the energy of interaction between the host framework and the distorted AgI_3^{2-} guest anion. Furthermore, the off-plane shift of Ag is favored by an absence of neighbors along the threefold axis, the nearest, As(2), lying 3.66 Å apart. The absence of near neighbors in the direction of the threefold axis can also explain the large amplitude of the thermal vibrations along this axis, which lowers upon cooling (Figure 4).

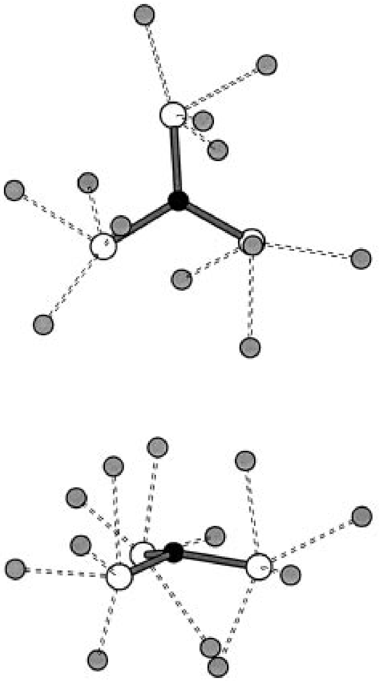

Figure 3. Coordination of the AgI_3^{2-} anion by the mercury atoms of the host framework; top: a view almost along the threefold axis; bottom: a side view; black circles, Ag; open circles, I; gray circles, Hg(1)

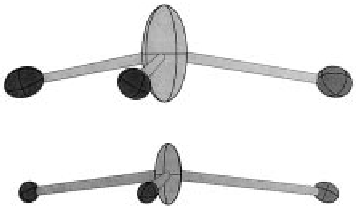

Figure 4. Thermal ellipsoids (50% probability) of the AgI_3^{2-} anion at 293 K (top) and 120 K (bottom); light gray, silver; dark gray, iodine

Experimental Section

Synthesis: A stoichiometric mixture of mercury(II) iodide, arsenic, silver powder, and liquid mercury (all > 99.99%; 0.5 g) was heated for 2 d at 775 K in a vacuum-sealed silica tube. Then, the ampoule was cooled down to 575 K and heated for further 2 d. A comparison of the diffraction pattern of the sample [STADI-P (STOE), Cu-$K_{\alpha 1}$ radiation] with the theoretical pattern calculated on the basis of the data obtained during the structure refinement revealed that the sample was almost phase-pure and had only a slight admixture of arsenic and Hg_2I_2.

Crystal Growth: Single crystals of the title compound were obtained by annealing a mixture of starting materials (3:4:2:3 molar ratio, total weight approx. 0.5 g) in a vacuum-sealed silica tube (60 mm length, 6 mm inner diameter) for 5 d at 675 K, and then cooling it down to ambient temperature at a rate of 30 K/h.

Crystal Structure Determination: For the ambient temperature experiment, a suitable single crystal of the reported compound was mounted on a CAD-4 (Nonius) goniometer head. The cubic unit-cell parameter was refined based on 24 well-centered reflections. The data collection parameters are listed in Table 3. A semiempirical absorption correction was introduced based on azimuthal scans of six reflections with χ angles close to 90°. The structure was solved by direct methods (SHELXS-97)[6] and refined anisotropically by a full-matrix least-squares method on F^2 (SHELXL-97)[6] to $R_1 = 0.0393$ and $wR_2 = 0.0839$. Final $\Delta\rho(xyz)$ synthesis revealed no chemically significant electron-density peaks. For the low-temperature structural investigations on the same single crystal, a data set was collected with a Bruker SMART 1000 CCD diffractometer at 120 K (Table 3). The absorption correction was applied by a standard routine (SADABS[10]). The crystal structure was refined (SHELXL-97,[6] anisotropic full-matrix least-squares refinement on F^2, $R1 = 0.0419$, $wR2 = 0.0905$) using the starting atomic positions determined in the previous experiment. Further details of the crystal structure determination may be obtained from Fachinformationzentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD-391131 and -391132.

Table 3. Data collection and structure refinement parameters for $[Hg_7As_4](AgI_3)_2$

Empirical formula	$Ag_2As_4Hg_7I_6$	
T [K]	293(2)	120(2)
Space group	$Pa\bar{3}$ (no. 205)	
Cell parameter a [Å]	13.138(1)	13.108(1)
V [Å^3]	2267.7(3)	2252.0(4)
Z	4	
Density (calcd.) [Mg/m^3]	7.853	7.907
μ [1/mm]	62.826	63.266
Crystal size [mm]	0.13 × 0.06 × 0.05	
Radiation, λ [Å]	Mo-K_α, 0.71069	
Data collection range [°]	$2.69 < \theta < 25.48$	$2.69 < \theta < 25.44$
Reflections collected	2123	6088
Independent reflections	707 [R(int) = 0.0944]	704 [R(int) = 0.0881]
Parameters refined	30	
R1,[a] $wR2$[b] [$F_o > 4\sigma(F_o)$]	0.0393, 0.0839	0.0419, 0.0905
R1, $wR2$ (all data)	0.0677, 0.0895	0.0595, 0.0952
Lagest diff. peak and hole [e/Å^3]	1.629 and −1.695	2.350 and −4.243
G.o.f. on F^2	1.047	0.947

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o||$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = \{\sigma^2(F_o^2) + A[(F_o^2 + 2F_c^2)/3]^2\}^{-1}$; $A = 0.0195$ (293 K), 0.0472 (120 K).

Thermal Properties: A small quartz ampoule was completely filled with compound (approx. 0.2 g). The ampoule was evacuated and sealed. The differential thermal analysis curve was recorded with a modified PRT-1000m device at a 10 °C/min heating/cooling rate.

Calculational Details

Band Structure Calculations: Extended Hückel calculations of the band structure were performed with the YAeHMOP[11] program package utilizing the built-in atomic parameters. A mesh of 41 k-points taken within the irreducible wedge of the Brillouin zone was used.

Molecular Calculations: RHF (including MP2[12] correlation correction) and DFT (BLYP, VWN, and B3LYP[13] exchange-correlation potentials) calculations were performed using the GAMESS-US[14] program. The SBKJC effective core potentials were applied to all atoms and the SBKJC basis set[15] implemented in GAMESS was used. The starting geometry of the AgI_3^{2-} anion was taken from the crystal structure refinement. Geometry optimizations were performed by the quasi-Newton algorithm implemented in GAMESS.

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