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Synthesis and the crystal structure of $[Hg_6As_4](InCl_6)Cl$: influence of covalent and electrostatic factors on the supramolecular structure

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A new inorganic supramolecular complex $[Hg_6As_4](InCl_6)Cl$ was synthesized. The complex crystallizes in the cubic space group $Pa3$ with the unit cell parameter $a = 12.109(1)$ Å and $Z = 4$. The crystal structure of the complex is based on the ${}^3_\infty[Hg_6As_4]^{4+}$ three-dimensional cationic host framework. The guest $InCl_6{}^{3-}$ and Cl^- anions are located in the cavities of the framework. The host—guest interactions were examined by quantum-chemical calculations of the equilibrium geometry of the $InCl_6{}^{3-}$ anion and analysis of the periodic zero-potential surface of the supramolecular complex. It was demonstrated that the electrostatic factors dominate over the covalent factors in the organization of the supramolecular structure of $[Hg_6As_4](InCl_6)Cl$.

Key words: inorganic supramolecular complexes, crystal structure, host—guest interactions, quantum-chemical calculations, periodic zero-potential surfaces.

Among inorganic supramolecular complexes[1] characterized by one-, two-, or three-dimensionally infinite host frameworks, ensembles based on frameworks consisting of the mercury and pnictogen atoms are of special interest.[2—9] Unlike most of inorganic supramolecular compounds, these ensembles generally show ordering not only of the host substructure but of the guest substructure as well.[2—7] Both components of these compounds, *viz.*, the guest and the host, are charged.

In the present study, we report the synthesis of a new inorganic supramolecular complex $[Hg_6As_4](InCl_6)Cl$, the description of its crystal structure, and examination of the electrostatic and covalent factors responsible for its structural characteristics.

Experimental

Synthesis. The $[Hg_6As_4](InCl_6)Cl$ complex was synthesized by the reaction of mercury(I) chloride (Aldrich), grey arsenic, and indium (the latter two compounds were of special purity grade) taken in the ratio corresponding to the following reaction

$$7\ Hg_2Cl_2 + 8\ As + 2\ In = 2\ [Hg_6As_4](InCl_6)Cl + 2\ Hg.$$

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A weighed sample (1 g) of a mixture of the starting compounds was placed in a quartz tube 6 cm in length (the inner diameter was 7 mm) and the tube was sealed *in vacuo*. The reaction mixture was tempered at 500 °C for 72 h, cooled to 300 °C, tempered at this temperature for 72 h, and then furnace-cooled. According to powder X-ray diffraction analysis (a Nonius FR-552 Guinier-de-Wolf camera, Cu-Kα_1 radiation) and visual observation, the resulting sample was a mixture of a new cubic phase with the unit cell parameter a = 12.110(1) Å and liquid mercury.

Crystal structure determination. Dark-red parallelepiped-shaped crystals ($0.13\times0.13\times0.08$ mm^3) were chosen from the reaction mixture and mounted on a goniometric head on a Nonius CAD-4 diffractometer (graphite monochromator, λ(Mo-Kα) = 0.71073 Å, ~20 °C, $\omega/2\theta$ scanning technique). The parameter of the cubic unit cell a = 12.109(1) Å was refined using 24 well-centered reflections in the θ angle range of 11.5—14.7°. The absorption correction was applied using azimuth scanning of nine reflections with the χ angles close to 90°. The observed systematic absences indicated the only possible space group *Pa*3 (No. 205). The structure was solved by direct methods, which allowed the location of the mercury and indium atoms. The positions of the arsenic and chlorine atoms were revealed from a series of subsequent difference Fourier syntheses alternated with cycles of the least-squares refinement. The final anisotropic refinement using 527 reflections converged to $R_1 = 0.0505$. The principal interatomic distances and bond angles are given in Table 1.* The calculations were carried out using the SHELX-97 program package.[10,11]

Calculations. Geometry optimization was carried out by quantum-chemical calculations with the restricted Hartree—Fock (RHF) method using the GAMESS-US program package.[12] The SBKJC, MINI, and HW basis sets and the MP2 correlation correction incorporated into the GAMESS-US program package were used. The experimental geometric parameters were used as the starting model of the $InCl_6^{3-}$ anion. The calculations were carried out both within the point symmetry group O_h and the lower-symmetry groups (C_{3v} and C_s). The results of geometry optimizations demonstrated that the equilibrium geometry does not deviate from the O_h symmetry. Subsequent normal vibration analysis did not reveal imaginary frequencies. This fact indicates that all states that were revealed are true minima.

The molecular orbitals of the $InCl_6^{3-}$ anion were calculated at the EHT level using the CACAO program package.[13] The orbital exponents and the ionization potentials were taken from the literature.[14] The calculations were carried out within the point symmetry group O_h with the use of the experimental In—Cl distance (see Table 1).

Calculations of periodic zero-potential surfaces and their visualization were performed using a set of standard mathematical and graphical applications.

Results and Discussion

The crystal structure of the $[Hg_6As_4](InCl_6)Cl$ complex is based on the three-dimensional positively charged $^3_\infty[Hg_6As_4]^{4+}$ framework. In the cavities of the framework, the anions of two types alternate with each other. The octahedral $InCl_6^{3-}$ anions occupy larger cavities and the monoatomic Cl^- anions are located in smaller cavities (Fig. 1). The framework is built of the arsenic atoms linked in the As_2 dumbbells and the mercury atoms, which form a distorted octahedral environment about the dumbbells. The As_2Hg_6 octahedra share all their vertices to form a perovskite-like structure, which is distorted due to deviation of the As(1)—Hg—As(2) angle (166.2°) from 180° (Fig. 2). The As—As (2.41 Å) and As—Hg distances (2.49—2.50 Å) are similar to those found in numerous mercury arsenide halides.[4—8,15—17] The first distance cor-

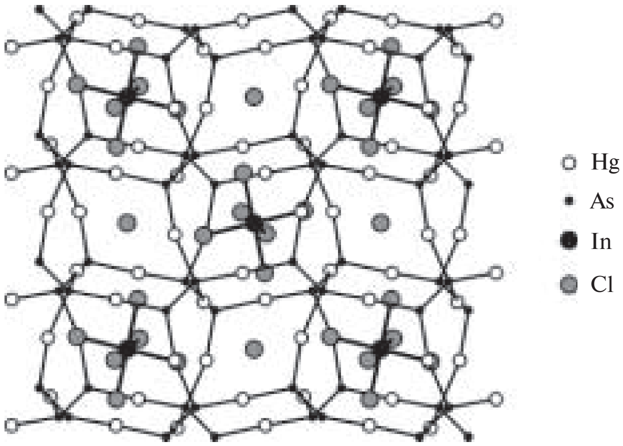

Fig. 1. Alternation of the $InCl_6^{3-}$ and Cl^- anions in the crystal structure of $[Hg_6As_4](InCl_6)Cl$.

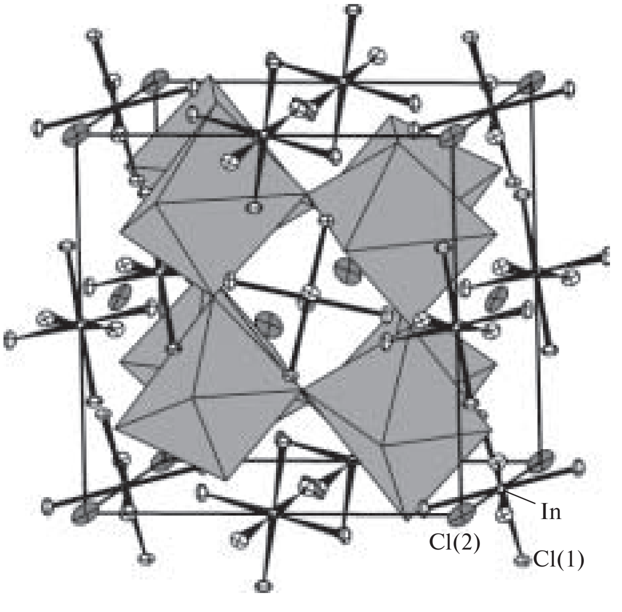

Fig. 2. Unit cell of the crystal structure of $[Hg_6As_4](InCl_6)Cl$. The $[Hg_6As_4]$ framework is represented by the vertex-sharing As_2Hg_6 octahedra. The In and Cl atoms are shown as ellipsoids drawn at the 50% probability level.

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* More detailed data on the study of the crystal structure can be obtained from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (*Fax:* +(49) 7247-808-666; *E-mail*: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD 411820.

responds to the single As—As bond and provides support for the fact that arsenic is in the formal oxidation state −2.

The $InCl_6^{3-}$ octahedron is virtually regular, *viz.*, all In—Cl distances are equal and the maximum deviation of the Cl—In—Cl angle from the octahedral value is no more than 1°. The In—Cl bond length (2.53 Å) falls within the range typical of the In—Cl distances observed in the $InCl_6^{3-}$ octahedra in the known compounds (2.41—2.66 Å).[18—21] The monoatomic Cl^- anion is characterized by the unusual coordination number of 14, all distances to the nearest neighboring atoms being substantially larger than the corresponding sums of the covalent radii (see Table 1).

Some other mercury and cadmium pnictide halides have analogous structures. Compounds containing both transition[6,22] and main-group[7] metals in the center of the octahedral MX_6^{3-} anion are isostructural to the $[Hg_6As_4](InCl_6)Cl$ complex. In contrast to the above-mentioned complexes, the larger cavities in the framework of the $[Cd_6P_4]CdCl_6$ complex are occupied by the octahedral $CdCl_6^{4-}$ anions, which completely compensate for the positive charge of the framework. The smaller cavities remain vacant.[23] In the structurally similar $[Hg_6As_4](HgCl_6)Hg_{0.4}$ complex, the smaller cavities are partially (by 40%) occupied by the zero-valent mercury atoms.[5]

The minimum distance between the mercury atoms of the framework and the Cl(1) (of $InCl_6^-$) and Cl(2) (Cl^-) atoms are 3.13 and 3.34 Å, respectively. Both distances are much larger than the Hg—Cl covalent bond length (2.27—2.29 Å).[24] Consequently, interactions between the framework (host) and the anions (guests) are noncovalent. Previously,[4] we have demonstrated that the host—guest interaction in the supramolecular $[Hg_7As_4I_3]SnI_3$ complex leads to deviation of the geometry of the guest SnI_3^- anion from the equilibrium geometry. In the present study, we also determined the equilibrium geometry of the guest $InCl_6^{3-}$ anion by *ab initio* calculations with different basis sets (Table 2). The geometry of the anion in the complex differs from the equilibrium geometry regardless of the calculation method used. In all cases, the calculated In—Cl bond length is approximately 0.1 Å larger than the experimental value, *i.e.*, the equilibrium $InCl_6$ octahedron in the cavity of the $[Hg_6As_4]$ framework is contracted.

Table 1. Interatomic distances and bond angles in the structure of $[Hg_6As_4](InCl_6)Cl$

Parameter	Value
Bond	*d*/Å
Hg—As(1)	2.494(1)
Hg—As(2)	2.498(1)
As(1)—As(2)	2.410(5)
In—Cl(1)	2.524(5)×6
Principal nonbonded distances	*d*/Å
Cl(1)—Hg	3.136(6)
Cl(2)—As(1)	3.223(4)×2
Cl(2)—Hg	3.3438(10)×6
Cl(2)—Cl(1)	3.740(5)×6
Bond angle	ω/deg
As(1)—Hg—As(2)	166.2(1)
Cl(1)—In—Cl(1)	180×3
Cl(1)—In—Cl(1)	90.9(1)×6
Cl(1)—In—Cl(1)	89.1(1)×6
As(2)—As(1)—Hg	109.74(8)×3
Hg—As(1)—Hg	109.20(8)×3
As(1)—As(2)—Hg	112.99(8)×3
Hg—As(2)—Hg	105.74(9)×3

Table 2. Calculated equilibrium In—Cl distances ($d_{In—Cl}$) in the $InCl_6^{3-}$ octahedron compared with those observed in the supramolecular $[Hg_6As_4](InCl_6)Cl$ complex

Method	$d_{In—Cl}$/Å
HW	2.614
MINI	2.622
SBK	2.648
SBK+MP2	2.640
Experiment*	2.530

* The value is taken from the crystal structure.

The molecular orbitals of the $InCl_6^{3-}$ anion were analyzed within the limits of the extended Hückel theory (EHT),[25] and HOMO of the anion was demonstrated to be the doubly degenerate antibonding orbitals e_g localized on the chlorine atoms (Fig. 3). Apparently, possible overlapping of these orbitals with the unoccupied orbitals (p_x and p_y) of the mercury atoms of the framework cannot lead to repulsive Cl(1)...Hg interactions, which would cause contraction of the $InCl_6$ octahedron. By contrast, one would expect weak attraction between the Hg and Cl(1) atoms separated by a distance of 3.13 Å because these atoms bear opposite charges.

To reveal the reasons for contraction of the $InCl_6^{3-}$ octahedron, we estimated the effect of the Coulomb forces on the distribution of the atoms in the crystal structure using the method of periodic zero-potential surfaces (POPS).[26] Analysis of the crystal structure (see Fig. 2) showed that the mutual arrangement of the isolated Cl^- anions and the As_2Hg_6 octahedra corresponds to the fluorite structural type. Following the principles of the math-

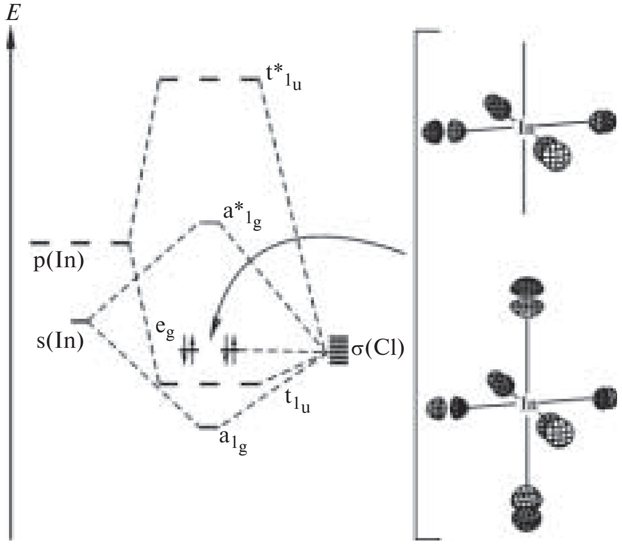

Fig. 3. Scheme of MO of the octahedral $InCl_6^{3-}$ ion and the shape of HOMO according to the results of EHT calculations.

ematical description of periodic surfaces,[27] we found that POPS of the CaF_2 structure is given by the following equation:

$$\cos 4\pi x + \cos 4\pi y + \cos 4\pi z + 4\cos 2\pi x \cdot \cos 2\pi y \cdot \cos 2\pi z = 0.$$

The surface size was scaled to match the unit cell parameter of $[Hg_6As_4](InCl_6)Cl$ (a = 12.109 Å), and then the positions of the atoms with respect to the periodic surface were calculated. Figure 4 demonstrates the surrounding of the Cl(2) atoms by the bubble-type surface. The atoms involved in the 14-atom coordination environment about the Cl(2) atom are located directly above this surface, the maximum deviation being 0.07 Å. It can be seen that the $[Hg_6As_4](InCl_6)Cl$ complex has the clathrate-like structure in which the Cl(2) atoms are located in the 14-vertex cage consisting of six Hg atoms, six Cl(1) atoms, and two As(1) atoms. The arrangement of these atoms corresponds to POPS, which limits the "sphere of influence" of the charge located on the $Cl(2)^-$ ion. On the

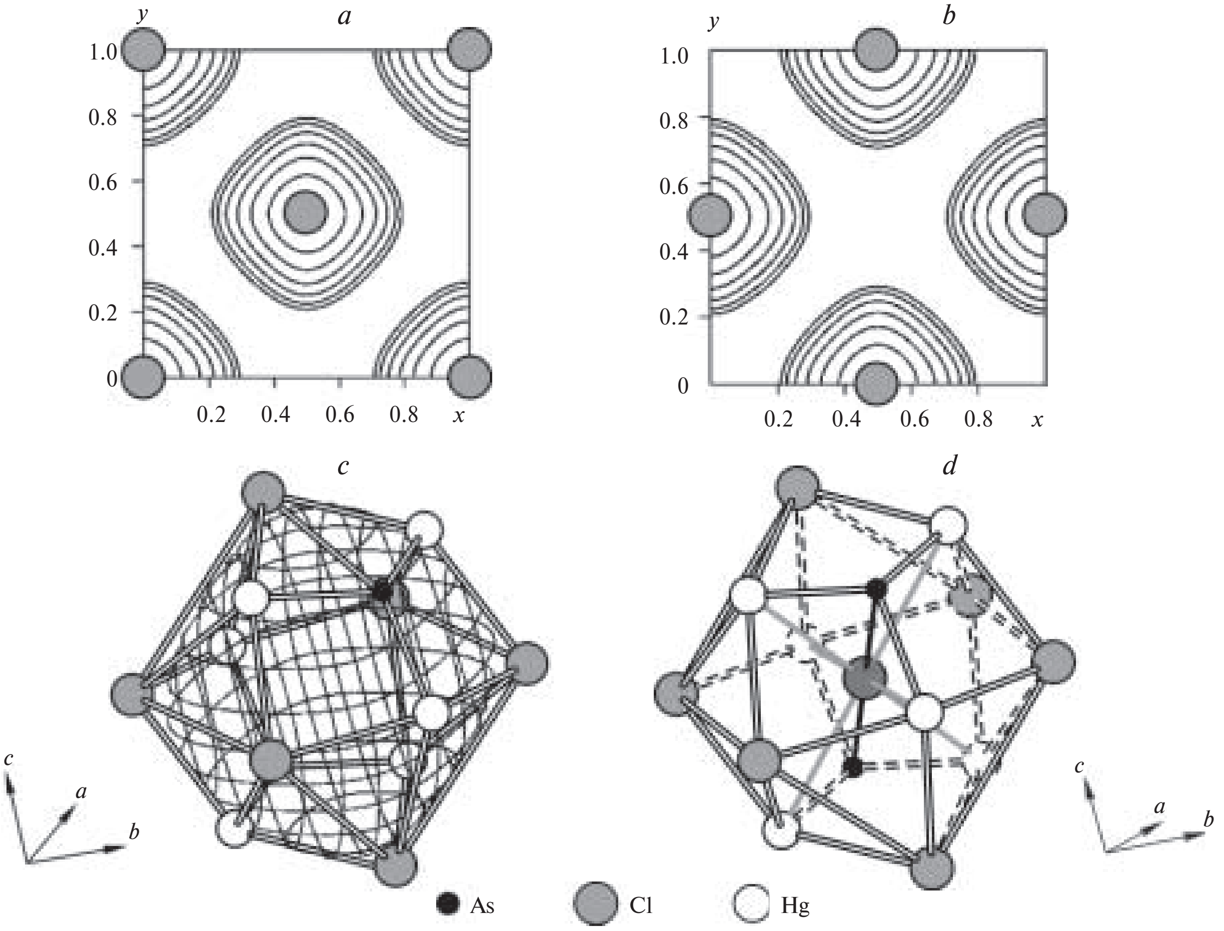

Fig. 4. The CaF_2-type periodic zero-potential surface and the $[Hg_6As_4](InCl_6)Cl$ structure; the contour diagrams of the surface within one unit cell at $z = 0$ (*a*) and $z = 0.5$ (*b*) (the contour intervals correspond to the increment $z = \pm 0.05$; the Cl(2) atoms are represented by shaded circles); the POPS fragment and 14 atoms, which are located above this fragment and are involved in the coordination sphere of the Cl(2) atom (*c*); the 14-vertex coordination polyhedron of the Cl(2) atom (*d*).

other hand, the calculated periodic zero-potential surface "does not allow" the Cl(1), Hg, and As(1) atoms to approach closer the Cl(2) atom, which is particularly essential for the Cl(1) atom because this is the reason for restriction of the In—Cl(1) distance in the octahedral $InCl_6^{3-}$ anion.

The results of the calculations demonstrate that the position of the Cl(1) atom is a compromise between the covalent and Coulomb forces. The forces of the first type cause the mutual repulsion between the Cl(1) atom and the In atom to the equilibrium distance, whereas the Coulomb forces, on the one hand, prevent the Cl(1) atom from intersecting POPS and, on the other hand, ensure a weak bond of the Cl(1) atom with the Hg atom as the coordination center of the guest located in the cavity of the host. Hence, it can be concluded that the electrostatic factors dominate over the covalent factors in the supramolecular structure of the $[Hg_6As_4](InCl_6)Cl$ complex.

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