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Metal-inorganic frameworks with pnictogen linkers

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Metal-inorganic frameworks are all-inorganic counterparts of well-known and extensively investigated metal-organic frameworks. Metal atoms connected by linkers form structures of different dimensionality with channels filled with atoms, ions or molecules. The review is devoted to metal-inorganic frameworks assembled from transition metal atoms, mainly mercury and silver, linked to phosphorus, arsenic or antimony atoms or groups of atoms of different shapes (dumbbells, rings, clusters, chains or helices). This assembly gives rise to frameworks of different geometry and with different topology. In all cases, the positively charged framework is composed of transition metal cations and pnictogen atoms as linkers. The positive charge of the framework is compensated by guest anions. Depending on the charge of the framework and the nature of the anion, compounds with different structures and properties can be produced. Specific features of metal-inorganic frameworks, the influence of weak interactions on the framework architecture and possibilities of designing new frameworks are discussed.
The bibliography includes 82 references.

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1. Introduction

One of the first studies,[1] in which a metal-organic framework was synthesized by the slow diffusion of benzene into an ammonia solution of $Ni(CN)_2$, was published in 1897. Several tens of publications dealing with such compounds appeared over the subsequent 100 years. Currently, these framemworks are the subject of over a thousand research papers per year. They are promising materials for gas storage, asymmetric and enantioselective catalysis, anion binding and exchange and so on. Metal-organic frameworks are assembled from metal ions or metal clusters connected by polyfunctional organic ligands (linkers) to form one-, two- or three-dimensional structures. The dimensionality of the framework depends on the denticity of the linker ligands. The framework structures can be formed with the involvement of template molecules or ions. The possibility of combining various coordination sites and linkers opens up great scientific and technological prospects.

Certain groups of inorganic compounds can be assigned to metal-inorganic frameworks (MIFs). These compounds retain all specific features of their organic counterparts — metal-organic frameworks. The main difference between these two classes of compounds is the nature of linkers. In most MIFs, inorganic clusters or polyanions, which have a rigid structure and contain several separated electron-donating atoms, serve as linkers.[2] Metal-inorganic frameworks are supramolecular assemblies always built up from charged components (so-called guests and hosts), which are connected in such a way as to ensure a compromise between complementary geometry, topology and charge. Most of these compounds are well-ordered solid crystals, which are unique subjects for investigating structure – property relationships in inorganic supramolecular systems.

Metal-inorganic frameworks based on various transition metals have been reported, but most of them contain derivatives of second and third row transition metals. This

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review describes supramolecular assemblies based on covalently bonded metal-pnictogen frameworks that incorporate guests of different complexity. The positively charged host framework is composed of linearly coordinated mercury or silver atoms and tetrahedrally coordinated pnictogen atoms.† Changes in the MIF structure required for the above-mentioned complementary compromise are described. The size matching of the framework cavities with the guest anions is evaluated based on the crystal-chemical data, in particular, from the changes in the bond lengths. Nanosized cavities of different shape are occupied by various guest anions, varying from halides to halometallate anions. Inside the framework, pnictogen atoms form linkers of different shape and with different charges — from a simple dumbbell, *e.g.*, $(As_2)^{4-}$, to cyclic anions, *e.g.*, $(P_8)^{8-}$ and $(P_{11})^{3-}$, and even 1D condensed anions, such as $^1_\infty(As_6)^{6-}$ and $^1_\infty(P_{10})^{3-}$. Metal-inorganic frameworks are considered in order of increasing complexity of inorganic linkers.

2. Dimensionality: from the simple to the complex

2.1. Millon's phases and their analogues

Millon's base and its salts, which have been known since the beginning of the 20th century,[3] can be considered as the simplest MIFs. The principles of their formation are very simple. The metal-inorganic framework of these compounds is composed of mercury atoms linearly coordinated by two nitrogen atoms, which are, in turn, in a tetrahedral environment formed by four mercury atoms. The framework bears a positive charge compensated by guest anions, thus ensuring the electroneutrality of the compound. An example is the complex $[Hg_2N]I \cdot H_2O$, which is often used for qualitative analysis. In the crystal structure of anhydrous $[Hg_2N]I$, iodide anions occupy channels of the three-dimensional $[Hg_2N]^+$ framework (Fig. 1 *a*). The mercury atoms have a linear coordination, and the nitrogen atoms are in a tetrahedral environment. The Hg_4N tetrahedra (Fig. 1 *b*) are linked together by sharing all vertices to form a tridymite-like framework, the cavities of which are occupied by iodide anions as guests. The crystal structures of Millon's base and its salts are also based on a the three-dimensional $[Hg_2N]^+$ framework composed of Hg_4N tetrahedra, with the guest anions occupying the cavities.[3, 4, 7, 8] In most cases, the frameworks are topologically related to the tridymite structure. Only the frameworks of the sulfate $[Hg_2N]_2SO_4 \cdot 2H_2O$ (Ref. 9) and nitrate of Millon's base[10] have a different topology: a cristobalite-like framework and a framework with a unique topology, respectively (the detailed information is given in Table 1). It should be noted that in tridymite-like frameworks, the channels run along one direction, whereas mutually intersecting channels run along three directions in cristobalite-like frameworks. Evidently, the geometry and topology of the crystal structure depend on the following two factors: the matching of the radius of the anion to the size of the cavitiy and the host–guest charge balance.

Other Group 15 elements are also prone to form four tetrahedral bonds. The replacement of the nitrogen atom by phosphorus, arsenic or antimony do not necessarily lead to a change in the framework topology, but a larger cavity size will require the presence of a bulkier guest anion for charge compensation. Thus, the I^- anion that is present as the guest in the $[Hg_2N]^+$ framework should be replaced in the $[Hg_2P]^+$ framework by tetrahedral anions of the general formula MX_4 to ensure the host–guest complementarity. One $(ZnI_4)^{2-}$ anion can be present in the tunnels of the mercury-pnictogen framework instead of a pair of iodide ions (Fig. 1 *c*). This gives rise to the crystalline compound $[Hg_2P]_2(ZnI_4)$ (Ref. 5) with the $[Hg_2P]^+$ framework that retains the tridymite-like topology. The compound $[Hg_2P](HgBr_4)$ has a similar structure,[11] but the channels in the framework are occupied by distorted and disordered $(HgBr_4)^{2-}$ tetrahedra instead of $(ZnI_4)^{2-}$ tetrahedra.

Phosphorus atoms can be replaced by larger arsenic atoms. In the crystal structure of $[Hg_2As]_2(ZnI_4)$, the geometry of the framework remains unchanged, while the positions of $(ZnI_4)^{2-}$ anions were not located.[13] The disorder of the anions was assigned to the mismatch between the sizes of the host and the guest, with the result that the anion can occupy different positions in the too large cavity. This assumption is confirmed by the formation of the well-ordered crystal structure of $[Hg_2As]_2(CdI_4)$.[14] The replacement of the $(ZnI_4)^{2-}$ anion in $[Hg_2As]_2(ZnI_4)$ by the bulkier isovalent analogue $(CdI_4)^{2-}$ relieves the mismatch between the host and the guest (see Table 1). This example shows

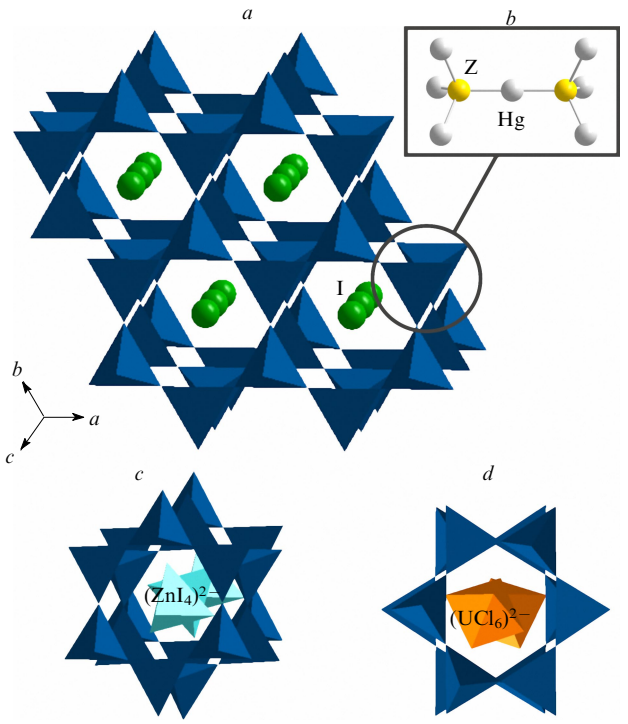


Figure 1. Polyhedral representation of the tridymite-like framework of salts of Millon's base and their analogues in relation to $[Hg_2N]I$ (*a*); the structure of the encircled Hg_4Z bitetrahedral unit (*b*), and schemes of the arrangement of tetrahedral anions in the channels of the tridymite-like framework in relation to $[Hg_2P](ZnI_4)$ (*c*) and octahedral anions in the channels of the tridymite-like framework in relation to $[Hg_2As](UCl_6)$ (*d*).
The Hg_4Z tetrahedra (Z = N, P, As) are shown in dark-blue. The data for the figure were taken from Ref. 4 (*a* and *b*), Ref. 5 (*c*) and Ref. 6 (*d*).

† In the review, the following abbreviations are used: Z is a pnictogen atom, X is a halogen atom.

Table 1. Selected structural data for Millon's phases and their analogues.

Compound	Type of the $[Hg_2Z]^+$ framework	Space group	M – X bond length in MX_4 or MX_6 /Å	Hg – Z bond length in the framework /Å	Ref.
$[Hg_2N]OH \cdot 2H_2O$ [a]	Cristobalite-like	$Fd\bar{3}m$	–	–	3
$[Hg_2N](NO_3)$	Unique structure	$P4_32_12$	–	2.037 – 2.081	10
$[Hg_2N]Br$	Tridymite-like	$P6/mmc$	–	2.045 – 2.111	7, 8
$[Hg_2N]I$	"	$P6/mmc$	–	2.045 – 2.111	4
$[Hg_2N]_2SO_4 \cdot H_2O$	Cristobalite-like	$F\bar{4}3m$	1.485 – 1.498	2.057	9
$[Hg_2P]_2(ZnI_4)$	Tridymite-like	$P2_1$	2.46 – 2.60	2.33 – 2.51	5
$[Hg_2P]_2(HgBr_4)$	"	$P2_1$	2.54 – 2.73	2.30 – 2.43	11
$[Hg_2P]_2(ZrCl_6)$	"	$Pbca$	2.438 – 2.483	2.377 – 2.413	12
$[Hg_2P]_2(HfCl_6)$	"	$Pbca$	2.437 – 2.467	2.360 – 2.431	12
$[Hg_2As]_2(ZnI_4)$ (see [a])	"	$P2_1$ or $P2_1/m$	–	2.33 – 2.51	13
$[Hg_2As]_2(CdI_4)$	"	$P2_1$	2.746 – 2.834	2.487 – 2.500	14
$[Hg_2As]_2(UCl_6)$	"	$Pbca$	2.605 – 2.639	2.462 – 2.485	6
$[Hg_2As]_2(ZrCl_6)$	"	$Pbca$	2.435 – 2.478	2.442 – 2.476	12
$[Hg_2As]_2(HfCl_6)$	"	$Pbca$	2.420 – 2.467	2.448 – 2.470	12
$[Hg_2Sb](GaCl_4)$	Cristobalite-like	$Pbnc$ (α)	2.144 – 2.182	2.665 – 2.671	15
		$P21cn$ (β)	2.665 – 2.671	2.668 – 2.687	15
$[Hg_2Sb](AlCl_4)$	"	$Pbnc$ (α)	2.07 – 2.13	2.656 – 2.694	16
		$P21cn$ (β)	2.656 – 2.694	2.668 – 2.686	16
$[Cd_2P]_2(CdBr_4)$	Tridymite-like	$Pna2_1$	2.529 – 2.723	2.40 – 2.45	17

[a] Only the model of the crystal structure is known.

that the host – guest complementarity is a driving force for the formation of MIFs.

Octahedral anions of appropriate size can also occupy the channels of tridymite-like $[Hg_2Z]^+$ frameworks. Several such compounds were described for quadruply charged metal cations, such as U^{4+}, Zr^{4+} and Hf^{4+}. The octahedral $(MCl_6)^{2-}$ anions (M = U, Zr, Hf) occupy cavities in the tridymite-like frameworks of the isostructural compounds $[Hg_2As]_2(MCl_6)$ (M = U, Zr, Hf) (Fig. 1 *d*),[6, 12] $[Hg_2P]_2(MCl_6)$ (M = Zr, Hf), resulting in an increase in the unit cell volume and higher symmetry. The well-known discrete octahedral $(UCl_6)^{2-}$ anion is a counterion for various organic cations, *e.g.*, $[N(CH_3)_4]^+$.[18] In all-inorganic compounds, this anion was found for the first time in $[Hg_2As]_2(UCl_6)$ and $[Hg_3Te_2](UCl_6)$.[6] The alkali metal compounds A_2UCl_6 (A = Li, Na, Cs) [19, 20] can be considered to contain $(UCl_6)^{2-}$ anions although the A – Cl distances in their structures are similar to the corresponding distances in simple chlorides.

2.2. Structural changes of Millon's phases upon the formation of Z – Z dumbbells

The question arises as to how the system responds to an increase in geometric incompatibility between the host and the guest stemming from an increase in the radius of the Group 15 element or a decrease in the size of guest anions. Compounds containing the $(ZnX_4)^{2-}$ anion (X = Cl, Br, I) provide clarity on this issue. These anions are invariably tetrahedral, with insignificant differences in the Zn – X bond lengths. For all X elements, compounds with Hg – As frameworks were prepared, two compounds with Hg – P frameworks were described, and one antimony-containing compound is known.

The above-described compound $[Hg_2As]_2(ZnI_4)$ is a tridymite-like analogue of Millon's phases. In this compound, the $(ZnI_4)^{2-}$ anions are small as compared to the cavities of the $[Hg_2As]^+$ framework, and the zinc positions are highly disordered. The $(ZnBr_4)^{2-}$ anions are even smaller in size, and either the $[Hg_2As]^+$ framework is too large to be formed around this template or this anion cannot be held in the framework cavity. As a result, the system responds in such a way as to decrease the size of the framework cavities by forming bonds between arsenic atoms. The resulting three-dimensional $[Hg_{23}As_{12}]^{12+}$ cationic framework is built up from two types of structural units: a Hg_4As tetrahedron similar to those forming the frameworks of salts of Millon's bases and their analogues, and a Hg_6As_2 trigonal prism with an arsenic dumbbell at the centre. The trigonal prisms and tetrahedra, which are present in a ratio of 1 : 10, share all vertices to form the $[Hg_{23}As_{12}]^{12+}$ framework (Fig. 2 *a*). The framework retains one-dimensional hexagonal tunnels running along the *c* direction similar to those in tridymite-like frameworks. The resulting compound has the formula $[Hg_{23}As_{12}](ZnBr_4)_6$.[13] Therefore, the $(ZnI_4)^{2-} \rightarrow (ZnBr_4)^{2-}$ transition is accompanied by a substantial mismatch of the framework. Thus, the simple $[Hg_2As]^+$ framework observed in the former case is transformed into a more complex one ($[Hg_{23}As_{12}]^{12+}$)

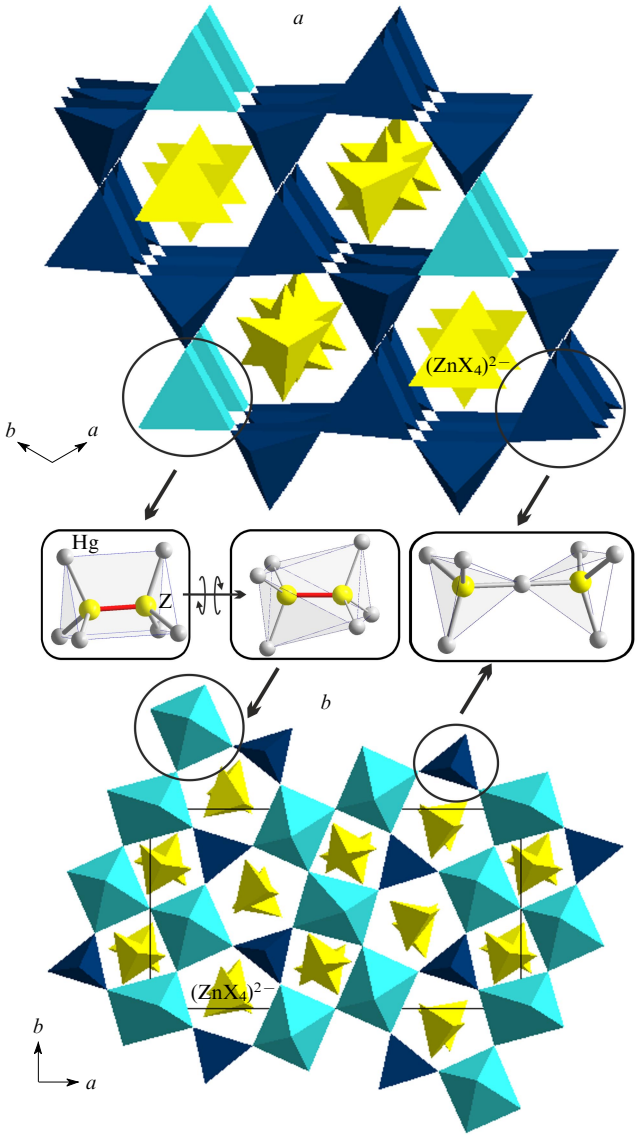


Figure 2. Polyhedral representation of the crystal structures of compounds with the $[Hg_{23}Z_{12}]^{12+}$ (Z = P, As) (*a*) and $[Hg_{13}Z_8]^{8+}$ (Z = As, Sb) (*b*) frameworks. The data for the figure were taken from Refs 13 and 21 (*a*) and Refs 13 and 22 (*b*).
The tetrahedral Hg_4Z structural units are shown in dark-blue; Hg_6Z_2 trigonal prisms, in blue; guest tetrahedral $(ZnX_4)^{2-}$ anions (X = Br, Cl), in yellow.

with smaller channels, allowing smaller guest anions to be accommodated. The replacement of the $(ZnBr_4)^{2-}$ anion by $(ZnCl_4)^{2-}$ necessitates a further contraction of the tunnels in the framework. The $[Hg_{23}As_{12}]^{12+}$ framework of the compound $[Hg_{23}As_{12}](ZnBr_4)_6$ is transformed into the $[Hg_{13}As_8]^{8+}$ framework of $[Hg_{13}As_8](ZnCl_4)_4$ (Fig. 2 *b*).[13]

An analysis of the two crystal structures demonstrated that a smaller number of dumbbells is required for the larger anion. In the bromine-containing compound, there is one $(As_2)^{4-}$ dumbbell per 10 arsenic atoms, whereas there are three dumbbells per two independent As^{3-} anions in the chlorine-containing phase. In the three-dimensional $[Hg_{13}As_8]^{8+}$ framework, the tunnels running along the *c* direction are retained, but, due to collapse of Hg_7As_2 bitetrahedra, some of these tunnels are pentagonal, while the other are tetragonal. The Hg_6As_2 structural units resulting from the collapse of the Hg_7As_2 bitetrahedra can rotate about the axis passing through the pnictogen atoms and adopt the shape of either trigonal prisms, like in the $[Hg_{23}As_{12}]^{12+}$ framework, or Archimedean antiprisms, like in the $[Hg_{13}As_8]^{8+}$ framework. It should be noted that the Hg_6As_2 Archimedean antiprisms are present as structural units in many mercury-pnictogen frameworks described below; in the literature, they are commonly described as distorted octahedra.

Evidently, the compound $[Hg_{23}P_{12}](ZnCl_4)_6$ (Ref. 21) is isostructural to the complex $[Hg_{23}As_{12}](ZnBr_4)_6$. The pairwise replacement of Cl atoms by Br and of As by Sb gives rise to the compound $[Hg_{13}Sb_8](ZnBr_4)_4$,[22] which is isostructural to $[Hg_{13}As_8](ZnCl_4)_4$.

2.3. Types of changes in the framework structure following a decrease in the charge of the guest anion

In the case of a change in the charge of the tetrahedral halometallate anion MX_4 from 2− to 1−, the number of the guest anions should be doubled in order to maintain the electroneutrality of the compound with the retenion of framework topology. The framework geometry should be changed to incorporate a larger number of anions. In most analogues of Millon's phases, the framework is built up from mercury and phosphorus (or arsenic) atoms and is topologically related to the tridymite structure. However, the cristobalite-like framework, in which the channels run along three directions, is apparently most suitable for the location of a large number of guest anions. The structure of Millon's phases can be preserved by combining mercury and antimony atoms in the cristobalite-like framework. Two isostructural compounds with the $[Hg_2Sb]^+$ framework — $[Hg_2Sb](GaCl_4)$ (Ref. 15) and $[Hg_2Sb](AlCl_4)$ (Ref. 16) — were synthesized. The tunnels in this framework are occupied by tetrahedral anions — $(GaCl_4)^-$ and $(AlCl_4)^-$, respectively (Fig. 3).

Larger cavities are required for larger anions, for example, in going from $(GaCl_4)^-$ to $(GaBr_4)^-$. In this case, the framework structures characteristic of salts of Millon's bases cannot be retained. Nevertheless, the compound $[Hg_6Sb_4](Ga_2Br_7)Br$ was synthesized in the Hg–Sb–Ga–Br system.[23] In this compound, the $[Hg_6Sb_4]^{2+}$ cationic framework is composed of mercury and antimony atoms, half of which form $(Sb_2)^{4-}$ dumbbells. Each dumbbell is surrounded by four mercury atoms to form the Sb_2Hg_4 unit unprecedented for this class of compounds. This unit is structurally similar to the distibane molecule Sb_2H_4 in a staggered conformation. The Sb_2Hg_4 units together with the bitetrahedral Sb_2Hg_7 structural units, in a ratio of 1 : 1, form the $[Hg_6Sb_4]^{4+}$ framework (Fig. 4). The crystal structure of one mercury pnictide halide with the composition $Hg_5I_6Sb_2$ (Ref. 24) contains the Hg_5Sb_2 structural unit derived by the removal of a mercury atom from one vertex of the Hg_6Sb_2 octahedron. To the best of our knowledge, this is the only example of inorganic compounds containing antimony atoms in the oxidation state 2−.

Therefore, the partial replacement of $SbHg_4$ tetrahedra by Sb_2Hg_4 in the cristobalite-like $[Hg_2Sb]^+$ framework leads to a change in the geometry of the cavities and elimination of the size inconsistency between the framework and guest anions. The $(GaBr_4)^-$ anions have a trigonal-bipyramidal structure formed by sharing axial vertices. The

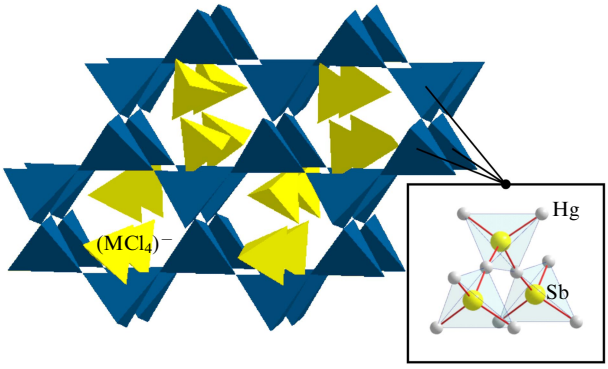


Figure 3. Overall view of the crystal structure of the compounds $[Hg_2Sb](MCl_4)$ (M = Al, Ga). The data for the figure were taken from Refs 15 and 16.
The Hg_4Sb tetrahedra that form the framework are shown in dark-blue; the guest tetrahedral $(MCl_4)^-$ anions, in yellow.

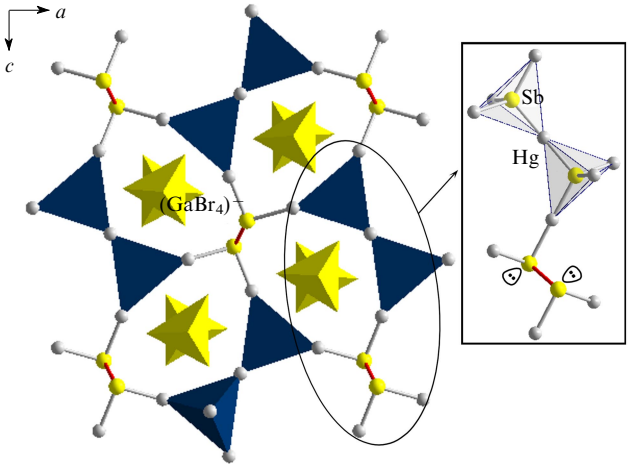


Figure 4. Overall view of the crystal structure of the compound $[Hg_6Sb_4](Ga_2Br_7)Br$. The data for the figure were taken from Ref. 23.

bipyramids are formed by bromine atoms, with the centres being occupied by two closely spaced gallium positions with half-occupancy. This disordered anion can be considered as $(Ga_2Br_7)^-$ bitetrahedra alternating with discrete bromide anions.

The compound $[Hg_{9.75}As_{5.5}](GaCl_4)_3$ (Ref. 22) is apparently structurally similar to $[Hg_6Sb_4](Ga_2Br_7)$. According to the authors, the electroneutrality of this compound is provided due to a decrease in the occupancy of the mercury positions and a complicated disorder of arsenic positions in the tridymite-like $[Hg_2As]^+$ framework, with $(GaCl_4)^-$ anions occupying the tunnels.

Evidently, the volume of the cavities decreases with increasing number of As–As dumbbells. The opposite effect is observed in the frameworks, in which isolated Hg^{2+} cations are replaced by linear $(Hg_2)^{2+}$ or even $(Hg_3)^{2+}$ polycations. For example, in the compound $[Hg_{11}As_4](GaBr_4)_4$,[25] pairs of $(GaBr_4)^-$ anions occupy the framework cavities, which are expanded due to the presence of linear $(Hg_2)^{2+}$ and $(Hg_3)^{2+}$ fragments (Fig. 5).

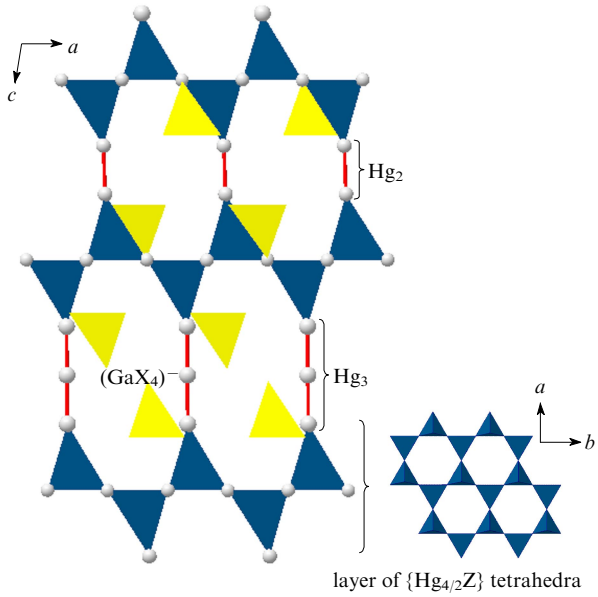


Figure 5. Overall view of the crystal structure of the compounds $[Hg_{11}Z_4](GaX_4)_4$ (Z = P, X = Cl; Z = As, X = Br). The data for the figure were taken from Ref. 25.

The $(GaBr_4)^-$ anion can be replaced by the $(GaCl_4)^-$ anion. In this case, the host–guest complementarity will be achieved by replacing arsenic atoms in the $[Hg_{11}As_4]^{4+}$ framework by phosphorus atoms, resulting in the formation of the compound $[Hg_{11}P_4](GaCl_4)_4$.[26] It should be noted that two compounds with the formulae Hg_2GaCl_4 and Hg_3GaCl_4 containing linear $(Hg_2)^{2+}$ and $(Hg_3)^{2+}$ cations were synthesized in the Hg–Ga–Cl system.[27] Evidently, this fact plays an essential role in the assembly of the complexes $[Hg_{11}P_4](GaCl_4)_4$ and $[Hg_{11}As_4](GaBr_4)_4$ described above. It is known that $(Hg_3)^{2+}$ cations can be stabilized by derivatives of strong Lewis acids, such as $[(MF_5)SO_4]^{2-}$ (M = Nb, Ta), $(AsF_6)^-$, $(AlCl_4)^-$.[28–30] Hence, it was suggested that new compounds with frameworks containing $(Hg_2)^{2+}$ and $(Hg_3)^{2+}$ units can be synthesized by using the above-mentioned anions.

Another distinguishing feature of $[Hg_{11}P_4](GaCl_4)_4$ and $[Hg_{11}As_4](GaBr_4)_4$ is that the shortest distances from the framework atoms to halogen atoms of the guest $(GaCl_4)^-$ and $(GaBr_4)^-$ anions are 3.478 and 3.669 Å, respectively. These distances are only slightly smaller than the sum of the van der Waals radii of mercury and halogen, but are substantially longer than the mercury–halogen covalent bonds (Tables 2 and 3). Nevertheless, the disorder of the guest anions is not observed in this structure.

2.4. Host–guest interaction

In host–guest complexes, the substructures are held together by noncovalent interactions of different strength — from hydrogen bonds or weak electrostatic interactions to van der Waals forces. Meanwhile, the bonds within the substructures are stronger. In most cases, the host and the guest are covalently bonded (more rarely, ionic) subsystems.[45] In the compounds under consideration, the framework is a covalently bonded three-dimensional network formed by pnictogen and mercury atoms. Covalent bonds (in some cases, with a rather large ionic component)

Table 2. Shortest distances from the framework mercury atom to halogen atoms of the guest anion.

Compound	Shortest Hg (framework) – X (guest) distance /Å	Ref.	Compound	Shortest Hg (framework) – X (guest) distance /Å	Ref.
α-$[Hg_2Sb](AlCl_4)$	3.210	16	$[Hg_8As_4]Bi_3Cl_{13}$	2.94	36
β-$[Hg_2Sb](AlCl_4)$	3.258	16	$[Hg_{11}P_4](GaCl_4)_4$	3.478	26
α-$[Hg_2Sb](GaCl_4)$	3.189	15	$[Hg_2N]Br$	3.325	4, 7
β-$[Hg_2Sb](GaCl_4)$	3.144	15	$[Hg_2P](HgBr_4)$	3.182	11
$[Hg_2P]_2(ZrCl_6)$	3.031	12	$[Hg_{23}As_{12}](ZnBr_4)_6$	3.056	13
$[Hg_2As]_2(ZrCl_6)$	2.991	12	$[Hg_{13}Sb_8](ZnBr_4)_4$	3.176	22
$[Hg_2P]_2(HfCl_6)$	3.184	12	$[Hg_6As_4Br_3](SnBr_3)$	3.049, 2.926 [b]	31
$[Hg_2As]_2(HfCl_6)$	2.967	12	$[Hg_6Sb_4](Ga_2Br_7)Br$	3.292	23
$[Hg_2As]_2(UCl_6)$	3.012	6	$[Hg_6As_4](CuBr_3)_2$	2.939	33
$[Hg_{9.75}As_{5.5}](GaCl_4)_3$	2.989	22	$[Hg_3Sb_2]TlBr_3$	2.874	35
$[Hg_{23}P_{12}](ZnCl_4)_6$	3.078	21	$[Hg_7(HgBr)_2As_4](Bi_2Br_{10})$	3.056	37
$[Hg_{13}As_8](ZnCl_4)_4$	2.874	13	$[Hg_{11}As_4](GaBr_4)_4$	3.669	25
$[Hg_6P_4Cl_3](SnCl_3)$	2.947, 2.814 [a]	31	$[Hg_2N]I$	3.365	4
$[Hg_6As_4Cl_3](SnCl_3)Hg_{0.13}$	3.009, 2.813 [a], 3.114 [b]	31	$[Hg_2P]_2(ZnI_4)$	3.421	5
$[Hg_6P_4Cl_3](PbCl_3)$	2.894, 2.854 [a]	21	$[Hg_2As]_2(ZnI_4)$	–	13
$[Hg_6P_4](CuCl_3)_2$	2.857	32	$[Hg_2As]_2(CdI_4)$	3.391	14
$[Hg_6As_4](CuCl_3)_2$	2.800	33	$[Hg_6Sb_4I_3](SnI_3)Hg_{0.16}$	3.204, 3.056 [a], 3.311 [b]	31
$[Hg_6As_4](AgCl_3)_2$	2.854	34	$[Hg_7As_4](AgI_3)_2$	3.310	38
$[Hg_3As_2]TlCl_3$	2.808	35	$[Hg_7As_4I_3](SnI_3)$	3.362	39
$[Hg_6P_3]In_2Cl_9$	3.04	36			

[a] The distances to additional halogen atoms incorporated into the framework.
[b] The Hg···X distances for guest mercury atoms.

Table 3. The Hg – X distances in mercury halides.

X	CN of mercury	Hg – X /Å		Ref.
		covalent bond	second coordination sphere	
Cl	2 + 6	2.27 – 2.29	3.37 – 3.48	40
Br	2 + 4	2.45 – 2.72	3.24	41
I [a]	2 + 4	2.63	3.52	42
I [b]	4	2.78 – 2.80	–	43, 44

[a] Orthorhombic (yellow) modification.
[b] Tetragonal (orange and red) modifications.

are present also between the atoms of the guest anion. The host and the guest are assumed to be connected by only weak, predominantly electrostatic, interactions. This description of compounds is confirmed primarily by the analysis of interatomic distances in the crystal structures (see Tables 1 and 2). The distances between the halogen atoms of the guest anion and the framework mercury atoms are longer than the covalent bonds in the corresponding mercury halides (see Table 3) but are smaller than the sum of the van der Waals radii of mercury and halogen (1.7 Å for mercury, 1.81 Å for chlorine, 1.91 Å for bromine, 2.15 Å for iodine).[46]

These distances correspond to secondary interactions in the related mercury halides, the number of these contacts being sufficient for the formation and stabilization of compounds.

In the $[Hg_{11}P_4](GaCl_4)_4$ and $[Hg_{11}As_4](GaBr_4)_4$ compounds described in the previous Section, the guest $(GaCl_4)^-$ and $(GaBr_4)^-$ anions form 6 or 9 mercury – halogen contacts with the framework. These multiple weak electrostatic interactions hold the tetrahedral anion within the cavity of the framework so that there is neither rotation of the anion nor displacement of the atoms, resulting in the absence of disorder. Electronic structure calculations by the density functional theory and the density-of-state analysis for the compound $[Hg_{11}P_4](GaCl_4)_4$ confirmed the presence of a strong covalent bond between the phosphorus and mercury atoms.[26] The electronic structure was considered in detail in relation to the $[Hg_2As]_2(CdI_4)$ complex.[14] The density-of-state analysis provides evidence that the arsenic 4p orbitals are mixed with mercury 6s orbitals, while iodine 5s orbitals are somewhat higher in energy than the 5s orbitals of cadmium. These data suggest that the Hg – As bond is covalent and that the Cd – I bond has a weak covalent character. The semiempirical population analysis gave a more accurate estimate of the bonding nature in this

compound and confirmed that the Hg–As bond is predominantly covalent, the Cd–I bond is predominantly ionic, and the Hg···I interaction is weak and diffuse in character. Consequently, the compound $[Hg_2As]_2(CdI_4)$ and related complexes can be described as salts with a three-dimensional polycation, the charge of which is distributed over the inner surface of the cavities and channels occupied by the guest anions.

Therefore, the framework of the complexes under consideration is assembled around the guest anions as a template. The framework atoms are coordinated around the cation *via* weak interactions and are simultaneously adapted to the geometry of the anion. This adaptation can be due to the following factors:

— change in the framework topology,

— decrease in the size of the channels upon the formation of dumbbells of Group 15 elements,

— expansion of the cavities due to the incorporation of linear mercury polycations.

The framework geometry can be controlled by selecting guest anions, which have a rigid geometry and bear a hardly changeable charge.

3. Two types of cavities in a single framework

3.1. Coordinated and clathrated guests

The replacement of all pairs of tetrahedra in the basic structure of Millon's base by Hg_6Z_2 structural units gives rise to the perovskite-like $^3_\infty[Hg_6Z_4]^{4+}$ framework. This framework can be represented as a four-connected network of pnictogen atoms topologically related to the γ-Si structure (Fig. 6 *a*), in which three of the four bonds are broken by mercury atoms (Fig. 6 *b*), but the cubic symmetry is retained. The concerted deviation of all Z–Hg–Z angles from 180° results in the formation of framework cavities of two different sizes in a ratio of 1 : 1 and provides a nearly regular tetrahedral coordination of pnictogen atoms (Fig. 6 *c*). We will refer to this framework as '64'.

There are more than 20 compounds having this type of framework. Most of these compounds crystallize in the cubic space group $Pa\bar{3}$ with the unit cell parameter *a* ranging from 12 to 13 Å (Table 4). The charge of the $[Hg_6Z_4]^{4+}$ framework should be compensated by the charges of the guest anions occupying the cavities. Large cavities are always occupied by octahedral halometallate anions MX_6, the charge of which determines the filling of the small cavities. In the case of trivalent metals, the guest MX_6 anion bears the charge 3–, and all small cavities are occupied by halide anions X^-, thus ensuring the electroneutrality of the complexes. The formula of the compounds can be written as $[Hg_6Z_4](MX_6)X$.[51–58] The presence of metal atoms in the oxidation state 3+ in the crystal structures of these phases was confirmed by the analysis of interatomic distances, magnetic susceptibility measurements and EPR spectra.[51–53, 56, 57]

Since the charge of the MX_6 anion formed by a divalent metal is already equal to 4–, which is necessary for the compensation of the framework charge, the small cavities are either not occupied or contain a certain amount of uncharged mercury atoms. The formula of such compounds can be written as $[Hg_6Z_4](MX_6)$ or $[Hg_6Z_4](MX_6)Hg_\delta$ (see Table 4). In these compounds, the larger cavities are occupied by octahedral anions $(Cd^{2+}X_6)^{4-}$ (X = Cl, Br, I), $(Hg^{2+}X_6)^{4-}$ (X = Cl, Br) and $(Fe^{2+}Br_6)^{4-}$.[48–51] In some compounds, the small cavities are partially occupied by mercury atoms. The latter are assigned an oxidation state of zero because of the coordination number 14 unusual for covalent compounds and rather large distances to the nearest neighbours (> 3.5 Å). This assumption is indirectly confirmed by the ^{199}Hg NMR spectra of the compound $[Hg_6As_4](HgCl_6)Hg_{0.4}$.[59]

The octahedral and monoatomic guest anions in the above-considered complexes have different coordination geometry. The octahedral MX_6 anions are located in the cavities confined by the framework mercury atoms. Each halogen atom of this anion is connected to four framework mercury atoms by weak interactions (Fig. 7 *a*).

The coordination sphere of the monoatomic guests, both halide anions in $[Hg_6Z_4](M^{3+}X_6)X$ and mercury atoms in $[Hg_6Z_4](M^{2+}X_6)Hg_\delta$, consists of six mercury atoms, six halogen atoms of the octahedral guest and two pnictogen atoms (Fig. 7 *b*,*c*). The distances vary from 3.30 to 3.87 Å. Taking into account the high coordination number and large interatomic distances, which are indica-

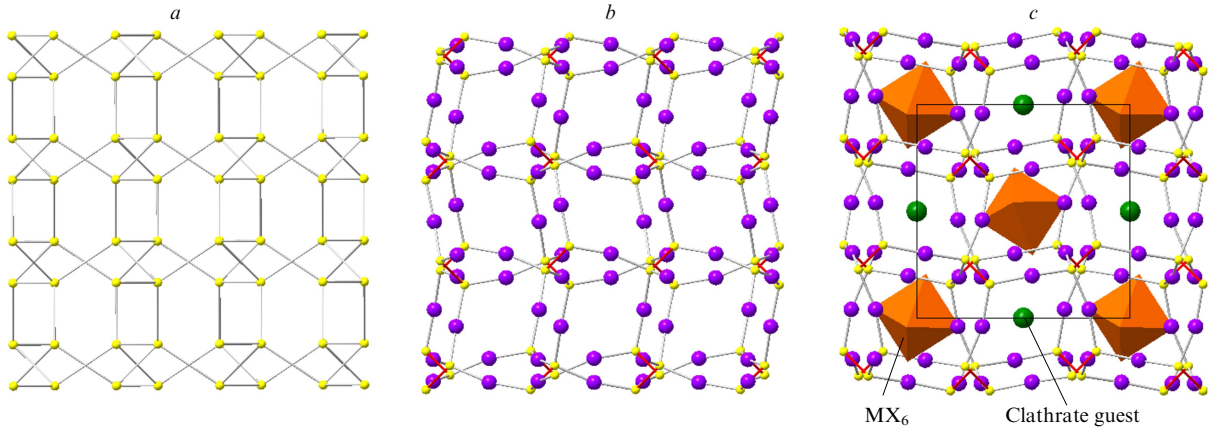


Figure 6. Structure of compounds with the $[Hg_6Z_4]^{4+}$ frameworks: the transformation of the topology of the γ-Si structure, sp.gr. $Ia\bar{3}$, (*a*) into the $[Hg_6Z_4]^{4+}$ framework, sp.gr. $Pa\bar{3}$ (*b*); an example of the structure containing two types of guests (the clathrated monoatomic guest is green; the octahedral halometallate anion is orange) (*c*). The data for the figure were taken from Ref. 47 (*a*) and Refs 47–58 (*b* and *c*).

Table 4. Compounds with $[Hg_6Z_4](MX_6)X$- or $[Hg_6Z_4](MX_6)Hg_\delta$-type frameworks incorporating two guests.

Compound	MX_6	M–X /Å	Shortest Hg–X distance /Å	Monoatomic guest	Unit cell parameter *a* /Å	Ref.
$[Hg_6As_4](CdBr_6)$	$CdBr_6$	2.806	3.021	–	12.374	48
$[Hg_6Sb_4](HgBr_6)$	$HgBr_6$	2.817	3.328	–	12.994	49
$[Hg_6As_4](CdCl_6)Hg_{0.5}$	$CdCl_6$	2.636	2.947	Hg^0 (50%)	12.172	48
$[Hg_6As_4](HgCl_6)Hg_{0.4}$	$HgCl_6$	2.704	2.937	Hg^0 (40%)	12.178	50
$[Hg_6As_4](HgCl_6)Hg_{0.5}$	$HgCl_6$	2.701	2.933	Hg^0 (50%)	12.189	48
$[Hg_6As_4](FeBr_6)Hg_{0.6}$	$FeBr_6$	2.672	3.045	Hg^0 (60%)	12.332	51
$[Hg_6Sb_4](CdI_6)Hg_{0.6}$	CdI_6	3.006	3.204	Hg^0 (60%)	13.234	48
$[Hg_6P_4](TiCl_6)Cl$	$TiCl_6$	2.420	3.064	Cl^-	11.762	52
$[Hg_6As_4](MoCl_6)Cl$	$MoCl_6$	2.443	3.121	Cl^-	12.078	53
$[Hg_6As_4](TiCl_6)Cl$	$TiCl_6$	2.440	3.135	Cl^-	12.094	53
$[Hg_6As_4](InCl_6)Cl$	$InCl_6$	2.525	3.136	Cl^-	12.109	54
$[Hg_6As_4](BiCl_6)Cl$	$BiCl_6$	2.705	3.112	Cl^-	12.178	55
$[Hg_6As_4](CrBr_6)Br$	$CrBr_6$	2.519	3.183	Br^-	12.275	51
$[Hg_6As_4](TiBr_6)Br$	$TiBr_6$	2.580	3.202	Br^-	12.309	53
$[Hg_6As_4](InBr_6)Br$	$InBr_6$	2.669	3.200	Br^-	12.351	56
$[Hg_6As_4](YbBr_6)Br$	$YbBr_6$	2.718	3.191	Br^-	12.362	57
$[Hg_6Sb_4](InBr_6)Br$	$InBr_6$	2.694	3.337	Br^-	12.854	56
		2.787	3.238	Br^-	12.962	58
$[Hg_6Sb_4](BiBr_6)Br$	$BiBr_6$	2.861	3.335	Br^-	12.998	55
$[Hg_6Sb_4](SbBr_6)Br$	$SbBr_6$	2.817	3.334	Br^-	13.003	55

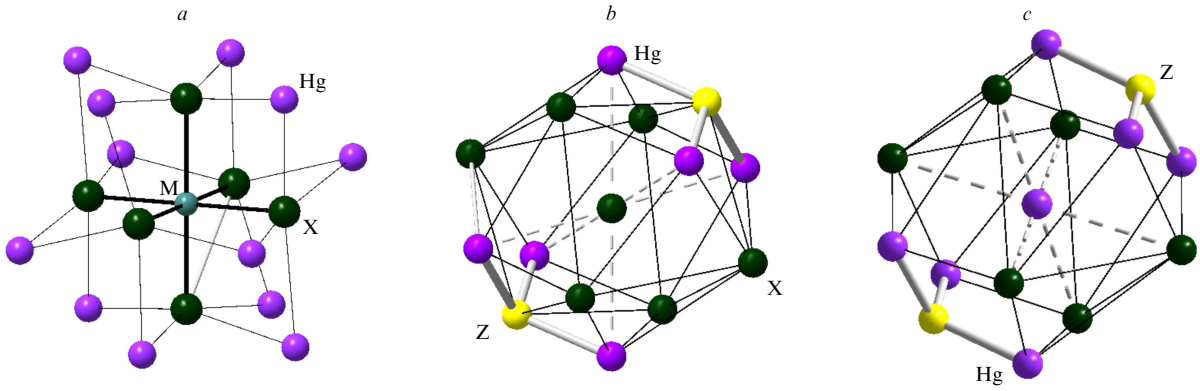


Figure 7. Coordination environment of the guest anions in the '64' frameworks: the octahedral MX_6 anion (*a*), the clathrated X^- (*b*) or Hg^0 (*c*) anion; the dashed lines indicate the shortest distances. The data for the figure were taken from Ref. 51.

tive of the absence of strong interactions, such guests are called clathrated. Besides, these guests have somewhat different coordination geometry depending on their nature. The largest distances from the clathrated guest to the neighbouring atoms always correspond to the separation of like charges, which attests to electrostatic repulsion. If a halogen atom is present as a guest, 6 mercury atoms in its coordination sphere are located at closer (although insignificantly) distances than the halogen atoms (Fig. 7 *b*). On the contrary, if mercury is a guest, 6 mercury atoms of the coordination sphere are the most remote ones (Fig. 7 *c*).

3.2. Mutual influence of host and guest

An analysis of the bond lengths in the crystal structures of compounds with $[Hg_6Z_4]^{4+}$ frameworks clearly demonstrated that strong covalent interactions can occur only within the host and guest substructures. The results of electronic structure calculations are consistent with the structural data.

The electronic structures of $[Hg_6Z_4](M^{2+}X_6)Hg_\delta$- and $[Hg_6Z_4](M^{2+}X_6)$-type compounds were calculated by the density functional theory without spin–orbit coupling. The calculations were performed for $[Hg_6As_4](CdCl_6)Hg_{0.5}$,

$[Hg_6As_4](HgCl_6)Hg_{0.5}$, $[Hg_6As_4](CdBr_6)$ and $[Hg_6Sb_4](CdI_6)Hg_{0.6}$.[48] In all these compounds, low-lying valence bands are composed of mercury d-orbitals or cadmium and mercury d-orbitals. The main contribution to the density of states in the band lying immediately below the Fermi level is from halogen and pnictogen p-electrons with an admixture of s-orbitals of the framework mercury atoms, whereas the conduction band lying immediately above the Fermi level is composed of mercury and cadmium s-orbitals and pnictogen p-orbitals. It should be noted that the contribution of the s-orbitals of mercury atoms serving as a clathrate guest is always substantially smaller than that of the mercury atoms occupying other positions. Clathrate mercury atoms are almost not involved in charge transfer. The optical absorbance of compounds can be described as charge transfer from halogen and pnictogen p-orbitals to s-orbitals of framework mercury atoms, sometimes with an admixture of s-orbitals of the metal centre of the octahedral guest anion. According to the electronic structure analysis and semiempirical bond population analysis, there are strong Hg–Z and Z–Z covalent bonds in the mercury–pnictogen framework. The degree of covalency in the framework is substantially higher for antimony compared to arsenic; the bonds in the halometallate anion have more ionic character. The interaction between the framework mercury atom and the halogen atom of the guest MX_6 anion is much weaker than those within the host and guest substructures.

The electronic structure of three-dimensional $[Hg_6Z_4](MX_6)X$-type metal-inorganic frameworks was studied in relation to the compound $[Hg_6P_4](TiCl_6)Cl$ by the extended Hückel tight-binding method (Fig. 8).[52]

In order to avoid overestimation of the contribution of the Hg–Cl orbit coupling between host and guest, the band structure of the compounds was calculated for the $[Hg_6P_4]^{4+}$ framework, while the molecular orbitals were calculated for the $(TiCl_6)^{3-}$ anion, the contribution of the second guest (Cl^- anion) being ignored because of its closed-shell electron configuration. The Hg_6P_2 octahedron is the main structural unit of the $[Hg_6P_4]^{4+}$ framework. The calculations performed previously for model $(Hg_6P_2)^{8+}$ cations demonstrated, in particular, that the highest occupied molecular orbital (HOMO) and orbitals lying immediately below the HOMO are composed mainly of π, π* and σ_z orbtials of the $(P_2)^{4-}$ dumbbell, which strongly interact with s-orbitals of six mercury atoms and with its d-orbitals. If considering the Hg_6P_2 octahedron involved in the $[Hg_6P_4]^{4+}$ framework, it is evident that the states lying immediately below the Fermi level retain their nature, the phosphorus p-orbitals and mercury s-orbitals making the dominant contribution to these states. A more important fact is that the mercury p-orbitals form a narrow band lying above the Fermi level but below the continuum. This band represents antibonding states localized on mercury atoms and it is a potential acceptor. The calculations demonstrated that the t_{2g} level of the $(TiCl_6)^{3-}$ anion is close in energy to that of the acceptor band. It should be noted that the t_{2g} molecular orbitals of Ti–Cl are π-antibonding and they are not localized on the titanium atom. Consequently, the transfer of the only unpaired electron can occur from the t_{2g} level to the acceptor band. Therefore, the host–guest interaction in the system under consideration is apparently determined by the charge transfer. The magnetic susceptibility values for $[Hg_6P_4](TiCl_6)Cl$ and other compounds containing the Ti^{3+} cation {$[Hg_6As_4](TiCl_6)Cl$ and $[Hg_6As_4](TiBr_6)Br$} correspond to localized d^1-centres ($\sim 1.8\ \mu_B$). This fact was interpreted in terms of spin–orbit coupling,[51] without the involvement of interactions in the host–guest system. However, this was not confirmed by EPR spectroscopy. Thus, the presence of a narrow line in the EPR spectrum of the compound $[Hg_6P_4](TiCl_6)Cl$ attests to an interaction between the host and guest substructures, resulting in an increase in the relaxation time and, consequently, in the excitation state lifetime.

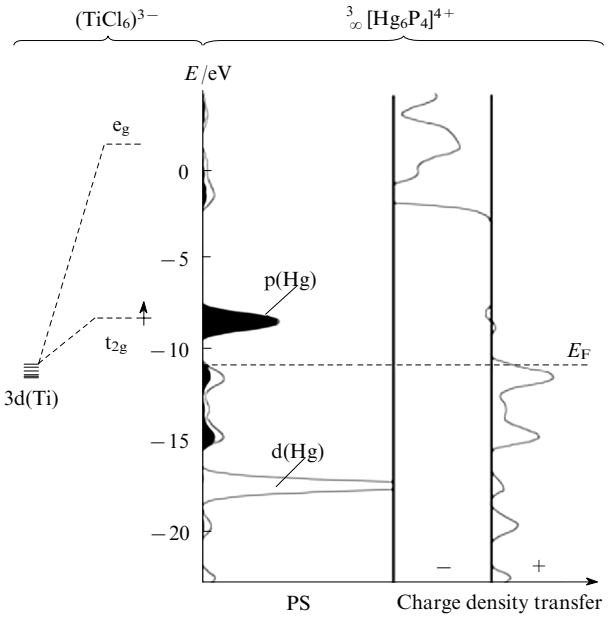


Figure 8. Charge transfer plot for the compound $[Hg_6P_4](TiCl_6)Cl$.
The contribution of mercury orbitals to the density of states (s + p) is highlighted in black.[52]

As shown by the example of $[Hg_6P_4](TiCl_6)Cl$, weak host–guest interactions can lead to some changes in the properties of the compounds. The same is possible for other transition metal compounds. The calculations demonstrated that numerous weak host–guest interactions in the complex $[Hg_6As_4](FeBr_6)Hg_{0.6}$ stabilize the low-spin t_{2g}^6 state of the Fe^{2+} cation (Fig. 9). This fact was confirmed by magnetic measurements, which showed that this compound is diamagnetic.[51] The magnetic moment of the chromium-containing compound $[Hg_6As_4](CrBr_6)Br$ ($3.34\ \mu_B$) is somewhat smaller than the calculated spin-only magnetic moment ($3.8\ \mu_B$). The EPR spectrum shows a very broad line,[51] which may also be indicative of the influence of the interaction in the host–guest system. Meanwhile, in the only compound containing an f-block element in the octahedral guest, $[Hg_6As_4](YbBr_6)Br$, weak host–guest interactions have no effect on the 4f electrons of the rare-earth element. The 4f orbitals are almost insensitive to the coordination environment of the rare-earth atom and are not involved in the direct binding between the central atom and the ligands, which occurs mainly due to filling of empty 5d- and 6s-orbitals of the ytterbium atom by electrons of the bromine atoms. Therefore, the magnetic moment of the $(YbBr_6)^{3-}$ anion is determined by the $4f^{13}$ configuration of ytterbium. The temperature dependence of the magnetic

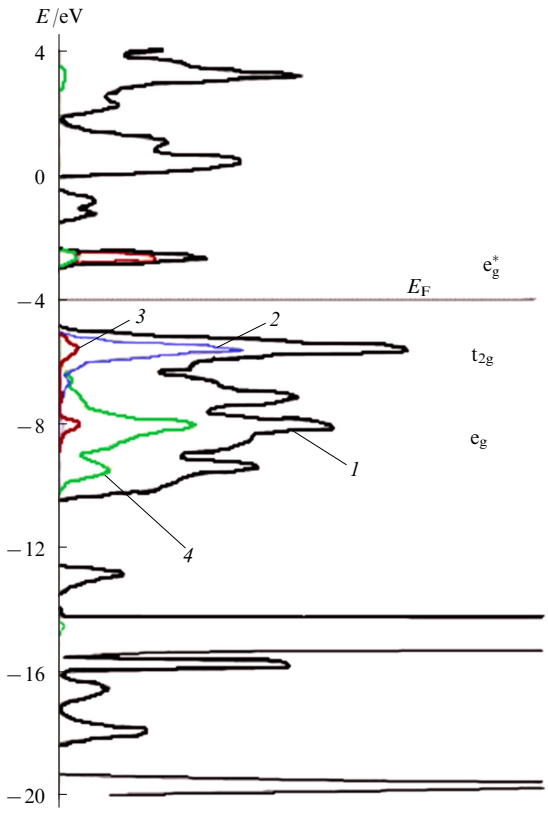


Figure 9. Density of electronic states for the compound $[Hg_6As_4](FeBr_6)$ calculated with the B3LYP hybrid functional.[51] The density of states: (*1*) total; for the d_{xy}, d_{xz}, d_{yz} (t_{2g}) (*2*) d_{z^2}, $d_{x^2y^2}$ (e_g) orbitals (*3*) of the iron atom and the p_z orbital (σ-type) (*4*) of the bromine atom.

susceptibility attests to the paramagnetic state of this compound.[57] Te effective magnetic moment is 4.47 μ_B, which is characteristic of the $^2F_{7/2}$ term of the ground state of the Yb^{3+} ion.

The influence of the host–guest interaction in the compound $[Hg_6As_4](InCl_6)Cl$ was analyzed.[54] The $(InCl_6)^{3-}$ octahedron has an almost regular shape: all In–Cl distances are equal, and the maximum deviation of the Cl–In–Cl angle is less than 1°. The In–Cl bond length is 2.53 Å. It was noted that this value is in the range characteristic of the corresponding distances in different compounds. However, *ab initio* calculations with different basis sets demonstrated that the structure of the anion in the complex differs from the equilibrium geometry, and the calculated In–Cl bond length is at least 0.1 Å larger than the experimental value. In order to reveal the factors responsible for the contraction of the $(InCl_6)^{3-}$ octahedron in the compound $[Hg_6As_4](InCl_6)Cl$, the periodic zero-potential surfaces (POPS) were calculated. The calculations demonstrated that the position of the chlorine atom of the guest $(InCl_6)^{3-}$ anion is a compromise between two types of interactions: covalent interactions, which cause the repulsion between the chlorine and indium atoms to the equilibrium distance, and electrostatic interactions, which, on the one hand, prevent the chlorine atom from intersecting the POPS and, on the other hand, provide a weak bond with the mercury atom serving as the coordination centre of the guest in the cavity of the host.

In the previous section, it was shown that the geometry of the framework depends on the nature of the anion. An analysis of numerous compounds with the $[Hg_6Z_4]^{4+}$ framework demonstrated its influence on the geometry and properties imparted by the guest anion. It should be noted that the size of the guest MX_6 anion in this type of compounds may be varied in a rather broad range; a slight deviation of its shape from the ideal octahedral geometry is also possible. The question arises as to why related compounds with other transition metals are absent. Octahedral guests should be considered as coordination units. Meanwhile, the octahedral shape of the guest anion is implied for the cavity of this framework. Taking into account that the structures of most of octahedral first-row transition metal coordination compounds are distorted due to Jahn–Teller effect, there is a limited number of potential guests. It is assumed that the existence of phases containing potentially labile transition metal ions is associated with the charge transfer mechanism. In this case, octahedral anions with filled e_g^* orbitals (M–X σ-antibonding) would donate electrons to the antibonding orbitals in the conduction band, thus destabilizing the electronic structure. This is why phases based on $[Hg_6Z_4]^{4+}$ frameworks, which contain octahedral MX_6 anions centred by doubly charged manganese, cobalt or nickel cations, are absent. The Co^{3+}, V^{2+} and V^{3+} ions cannot be included in these systems because of redox processes. The formation of compounds containing Hg^{2+}, Cd^{2+}, In^{3+} or Sb^{3+} at the centre of the octahedral guest is attributed to the fact that the low-lying d-levels — d^{10} and d^0 — of these cations do not split in the ligand field to a substantial extent.

3.3. Polymeric guest anions. Distortion of the $[Hg_6Z_4]^{4+}$ framework

The lowering of symmetry of the $[Hg_6Z_4]^{4+}$ framework due to deviations of Z–Hg–Z bond angles from ideal values for some atoms results in that all framework cavities become equivalent, whereas the framework in the above-described compounds $[Hg_6Z_4](MX_6)X/Hg_\delta$ contains more symmetric cavities of two types. The difference in the topology of the frameworks corresponds to their different hierarchical origin. A framework containing identical cavities is generated from a four-connected network of pnictogen atoms topologically related to the lonsdaleite structure,[60] in which mercury atoms are inserted into three of the four bonds (Fig. 10). A change in the topology of the $[Hg_6Z_4]^{4+}$ framework with the retention of the connectivity allows polymeric anions to occupy the cavities.

The compounds $[Hg_6As_4](CuBr_3)_2$, $[Hg_6As_4](CuCl_3)_2$,[33] $[Hg_6P_4](CuCl_3)_2$ (Ref. 32) and $[Hg_6As_4](AgCl_3)_2$ (Ref. 34) contain one-dimensional infinite six-step helical $^1_\infty[MX_3]^{2-}$ guest chains (M = Cu, Ag; X = Cl, Br) built up from vertex-sharing tetrahedra MX_4 (Fig. 11).

Although copper halides are characterized by the formation of various polyanions and clusters, the above type of anions were not found in copper-containing coordination polymers,[61] while silver tends to form clusters or isolated moieties, such as $[Ag(PBn_3)_2]_8[AgCl_3]Cl_6 \cdot 6H_2O$ (PBn_3 is tribenzylphosphine).[62]

It should be noted that the $^1_\infty[MX_3]^{2-}$ polyanions in the complexes $[Hg_6As_4](CuBr_3)_2$ and $[Hg_6As_4](AgCl_3)_2$ are fully ordered. Two free halogen atoms of each MX_4 tetrahedron each form three contacts with framework mercury atoms at distances corresponding to the second coordination sphere

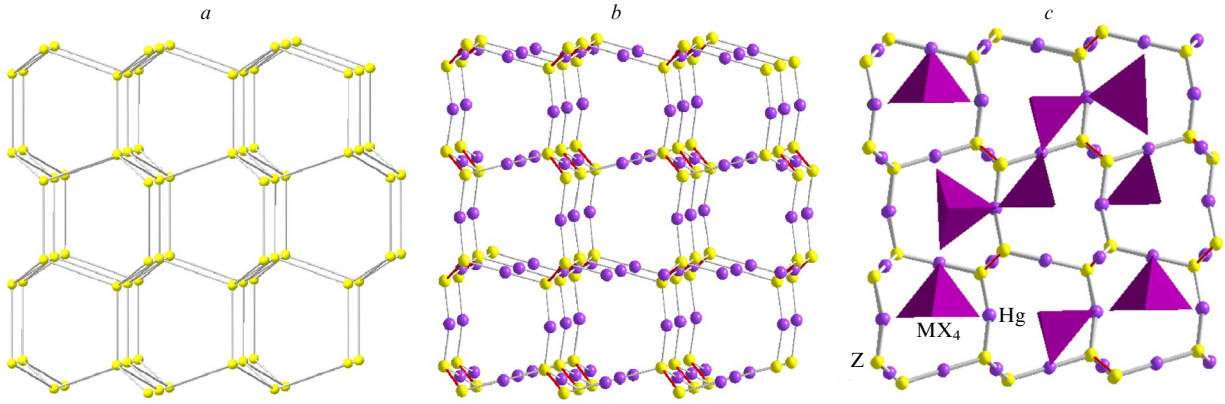


Figure 10. Structures of compounds with $[Hg_6Z_4]^{4+}$ frameworks: the transformation of the lonsdaleite structure (*a*) into the observed $[Hg_6Z_4]^{4+}$ framework (Z = P, As) (*b*) and an example of the arrangement of the polymeric guest $(M_2X_6)^{4-}$ anion (M = Ag, Cu; X = Cl; Br) in the framework (*c*). The data for the figure were taken from Refs 34 and 60.

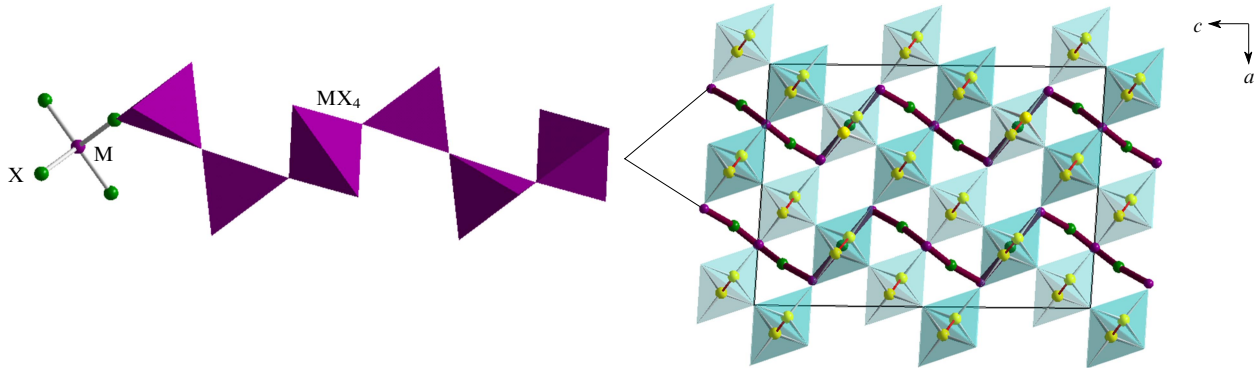


Figure 11. Structure of the anionic moiety in the compounds $[Hg_6Z_4](MX_3)_2$ and its arrangement in the $[Hg_6Z_4]^{4+}$ framework (Z = As; M = Ag, X = Cl; M = Cu, X = Cl, Br). The data for the figure were taken from Refs 32–34.

in mercury halides. By contrast, the substructures of the guest anions in the compounds $[Hg_6As_4](CuCl_3)_2$ and $[Hg_6P_4](CuCl_3)_2$ are disordered. In the former case, anionic chains have four different orientations. In the latter case, the character of disorder was elucidated by studying the crystal structure at 120 and 300 K. The copper positions split with decreasing temperature, the thermal displacement parameters of chlorine atoms being still several times larger than those of the framework atoms, which may be indicative of the dynamic character of guest disorder. It was hypothesized that the compound undergoes a ferroelectric phase transition at 37 K. At this temperature, changes are observed in the temperature dependences of dielectric permittivity and heat capacity, as well as in powder X-ray diffraction patterns. Structural transformations that occur at this temperature are poorly understood; however, it was established that the crystal structure experiences changes.

Complexes with mercury–pnictogen frameworks and two-dimensional infinite anions are unknown. The formation of three-dimensional guest anions can be discussed for two isostructural compounds — $[Hg_3As_2]TlCl_3$ and $[Hg_3Sb_2]TlBr_3$.[35] The crystal structures of these complexes, like the above-described compounds with one-dimensional infinite $_{\infty}^{1}[MX_4]^{2-}$ guest anions, have the positively charged $[Hg_6Z_4]^{4+}$ host framework containing cavities of equivalent shape and size. The anionic moieties in the compounds $[Hg_3As_2]TlCl_3$ and $[Hg_3Sb_2]TlBr_3$ can be described as TlX_6 octahedra (X = Cl, Br), which are connected together *via* sharing all vertices to form a perovskite-like sequence. The Tl–Cl and Tl–Br distances are similar to the corresponding distances in some mixed thallium halides, whereas the Hg–Cl and Hg–Br distances are much longer than those in mercury halides. The crystal structures of these compounds can be considered as two interpenetrating perovskite-like networks. Electronic structure calculations of the compounds and the population analysis of atomic orbital overlap demonstrated that the antibonding states lying immediately above the Fermi level in the bond between the thallium and halogen atoms are partially occupied, resulting in the loosening of the bonds. The same situation, though to a lesser extent, is observed for the mercury–halogen bond. The populations of atomic orbital overlap for Tl–X are two times smaller than those for Hg–X and are almost 10 times smaller compared to the merury–pnictogen bond. Therefore, the structure of these compounds can be described as a mercury–pnictogen framework with a charge delocalized over the inner surface and with trapped Tl^+ and X^- ions; the formulae can be written as $[Hg_3As_2]^{2+}(Tl^+)(Cl^-)_3$ and $[Hg_3Sb_2]^{2+}(Tl^+)(Br^-)_3$.[35]

Unusual compounds reported by Greiwe[63] contain halogen molecules as discrete guest moieties in two interpenetrating three-dimensional networks (cationic

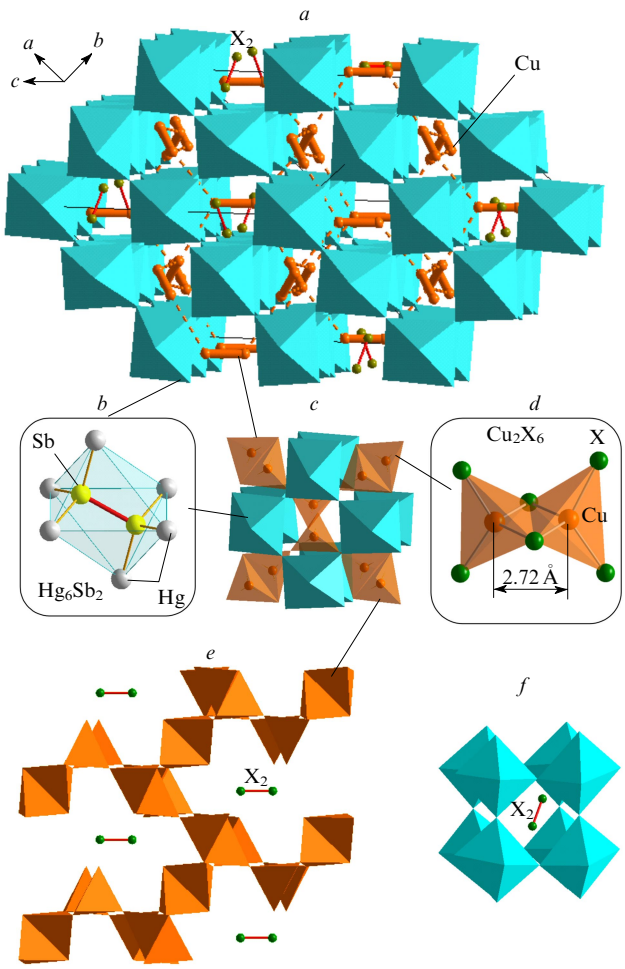


Figure 12. Overall view of the crystal structure of $[Hg_3Sb_2]_4(CuX_3)_4(X_2)$ (X = Br, I) (*a*), Hg_6Sb_2 octahedra (*b*), the arrangement of Cu_2X_6 bitetrahedra in the framework cavities (*c*), the Cu_2X_6 tetrahedron (*d*), the anionic substructure of Cu_2X_6 and X_2 molecules (*e*), the arrangement of X_2 molecules in the framework cavities (*f*). The data for the figure were taken from Ref. 63. (*a*) For the sake of simplicity, the Cu_2X_6 bitetrahedra are represented as Cu–Cu dumbbells, and the formation of the anionic substructure is indicated by dashed lines.

and anionic). Two isostructural complexes $[Hg_3Sb_2]_4(CuX_3)_4(X_2)$ (X = Br, I) were found when searching for new antimonides using mercury halides as transport agents. The compounds $[Hg_3Sb_2]_4(CuX_3)_4(X_2)$ have a unique structure. The $[Hg_6Sb_4]^{4+}$ framework is penetrated by a three-dimensional $\{Cu_2X_6\}^{4-}$ anionic network; the remaining free framework cavities are occupied by halogen molecules X_2 (Fig. 12 *a*). The $[Hg_6Sb_4]^{4+}$ cationic substructure is composed of distorted Hg_6Sb_2 octahedra centred by antimony dumbbells (Fig. 12 *b*). The structures of these compounds contain two types of such polyhedra, which are connected together *via* sharing all vertices to form the $[Hg_6Sb_4]^{4+}$ cationic framework. The $[Hg_6Sb_4]^{4+}$ framework in the compounds $[Hg_3Sb_2]_4(CuX_3)_4(X_2)$ differs from the frameworks derived from '64' or lonsdaleite in that it contains two types of cavities in a ratio of 3 : 1. The large cavities are somewhat elongated along the *ac* diagonal, while the small cavities are nearly spherical in shape. The large cavities are occupied by Cu_2Br_6 bitetrahedra (Fig. 12 *c*,*d*), which are linked to each other in the *ab* plane to form six-membered rings, resulting in the formation of a three-dimensional network that penetrates the $[Hg_6Sb_4]^{4+}$ framework (Fig. 12 *f*). The Cu–Cu distances in the bitetrahedron (Fig. 12 *d*) are comparable with the corresponding distances in the CuBr high-pressure modification (2.78 Å);[64] the occupancy of the copper positions is 2/3. It was argued that the cage occupied by the Cu_2Br_6 bitetrahedron causes the latter to be contracted, resulting in a decrease in the Cu–Cu distance. It was supposed that the small cavities are occupied by bromine or iodine dumbbells (Fig. 12 *f*) rotating about a threefold axis.

In the compound $[Hg_3Sb_2]_4(CuBr_3)_4(Br_2)$, the distance between the bromine atoms in the dumbbells is 2.23(2) Å, which is consistent with the corresponding distances in the $[C_4MPyr]_2[Br_{20}]^{2-}$ anion (2.29–2.34 Å)[65] and the bromine molecule (2.301 Å).[66] Meanwhile, in the isostructural compound $[Hg_3Sb_2]_4(CuI_3)_4(I_2)$, the I–I distance in the dumbbells is as short as 1.35(7) Å. These iodine atoms have abnormally high displacement parameters, and the distances from these atoms to the iodine atoms of the three-dimensional $(Cu_2I_6)^{2-}$ polyanion are rather short [3.59(4) Å]. Evidently, further investigations of the crystal structure of this compound are needed. The composition of the compound $[Hg_3Sb_2]_4(CuBr_3)_4(Br_2)$ calculated from the structural data is in agreement with the results of electron-probe X-ray microanalysis. It should also be noted that the complexes $[Hg_3Sb_2]_4(CuX_3)_4(X_2)$ are unstable under mechanical action and decompose under modest pressure with elimination of elemental halogens.

3.4. Pyramidal guest anions. Additional halogen atoms in the framework

Compounds with polymeric guest $^1_\infty[AgX_3]^{2-}$ anions (X = Br, I) isostructural to $[Hg_6As_4](AgCl_3)_2$ were not synthesized; however, the compound of the composition $[Hg_7As_4](AgI_3)_2$ was found in the Hg–As–Ag–I system.[38] This compound contains discrete $(AgI_3)^{2-}$ anions in the cavities of the $[Hg_7As_4]^{4+}$ framework (Fig. 13 *a*). The $[Hg_7As_4]^{4+}$ framework is composed of linearly coordinated mercury atoms and tetrahedrally coordinated arsenic atoms and can be described as a result of combination of two types of structural units connected to each other. The octahedral (Hg_6As_2) units and bitetrahedral (Hg_7As_2) units alternate with each other in a ratio of 1 : 1 (Fig. 13 *a*,*b*) and form a symmetrical framework with closed ellipsoidal cavities occupied by $(AgI_3)^{2-}$ anions. The $(AgI_3)^{2-}$ anion adopts a trigonal-pyramidal geometry (the I–Ag–I angles are 117.5°, all Ag–I bond lengths are equal). The silver atom is displaced from the plane passing through the iodine atoms by 0.41 Å. However, calculations of the equilibrium geometry of the $(AgI_3)^{2-}$ anion at different levels of theory by the restricted Hartree–Fock method and the density functional method demonstrated that the $(AgI_3)^{2-}$ anion should be planar. The deviation of the shape from the calculated planar conformation is attributed to the fact that the $(AgI_3)^{2-}$ anion is located in a cage formed by 12 mercury atoms (Fig. 13 *d*). It should be emphasized that this type of anions is unprecedented. Thus, only one compound containing the isolated $(AgI_3)^{2-}$ anion — $[PPh_3Me]_2(AgI_3)$ — was reported.[67] The interactions between the framework and the guest anion were qualitatively estimated by band structure calculations. The Hg–I interactions are weak and diffuse compared to strong

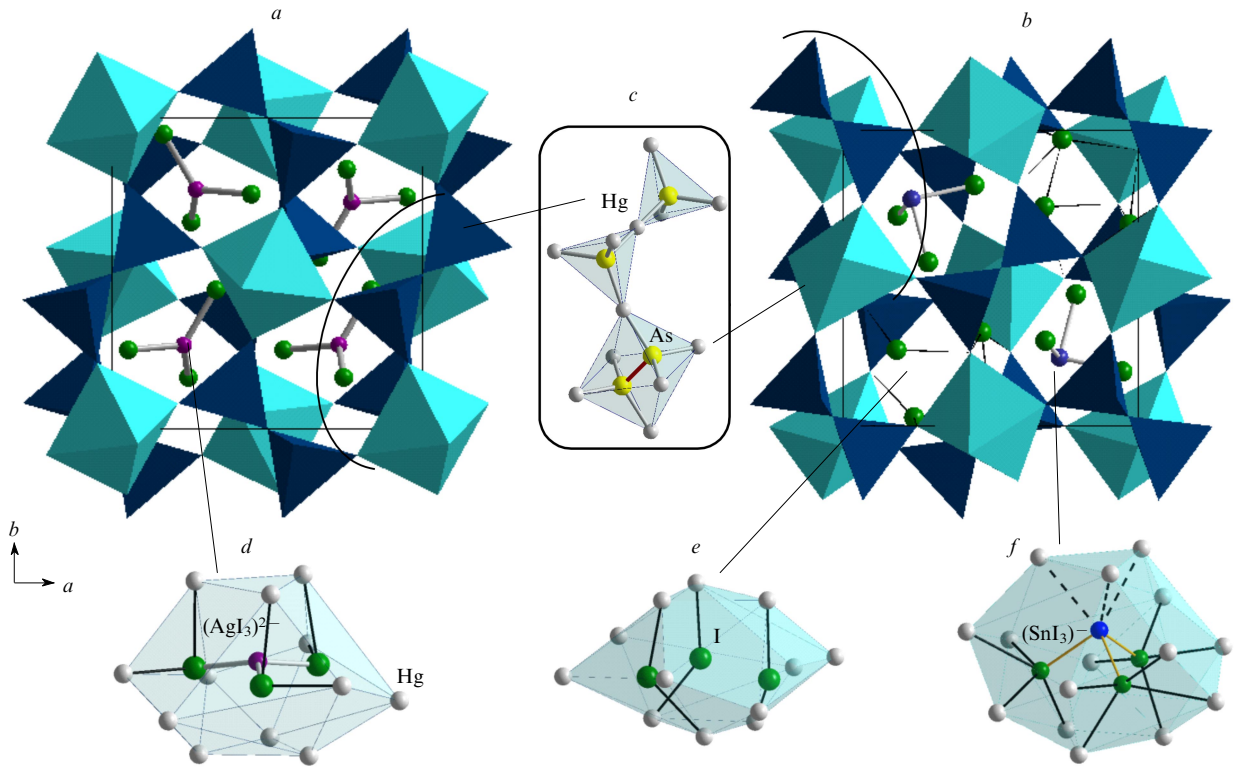


Figure 13. Overall view of the crystal structures with the guest $(AgI_3)^{2-}$ and $(SnI_3)^-$ anions. The data for the figure were taken from Ref. 38 (*a*) and Ref. 39 (*b*).
(*a*) $[Hg_7As_4](AgI_3)_2$; (*b*) $[Hg_7As_4I_3](SnI_3)_2$; (*c*) the formation of Hg_6As_2 polyhedra (light blue) and Hg_7As_2 polyhedra (dark blue); filling of the cavities in the frameworks formed by mercury atoms: (*d*) the guest $(AgI_3)^{2-}$ anion (black lines indicate the I···Hg distances < 3.5 Å), (*e*) iodine atoms occupying the small cavity; (*f*) the guest $(SnI_3)^-$ anion (black lines indicate the I···Hg distances < 4 Å).

Hg—As, As—As and Ag—I interactions within the host and guest substructures. This is additionally confirmed by the analysis of interatomic distances in the crystal structure, in which the bonds within the $[Hg_7As_4]^{4+}$ framework and the guest $(AgI_3)^{2-}$ anion correspond to covalent bonds, while the Hg···I distances are characteristic of the second coordination sphere of mercury atoms (see Tables 2 and 3).

The cavities of the $[Hg_7As_4]^{4+}$ framework can be occupied by other trigonal-pyramidal anions. For example, the $(AgI_3)^{2-}$ anion can be replaced by $(SnI_3)^-$, which will require the doubling of the number of anions in the cavities of the $[Hg_7As_4]^{4+}$ framework. However, two $(SnI_3)^-$ anions cannot be trapped for geometric reasons, and the system is adapted not *via* the rearrangement of the framework accompanied by an increase in the cavity size, but by incorporating additional iodine atoms that compensate the charge of the framework. This gives rise to the compound $[Hg_7As_4I_3](SnI_3)$ [39] with a framework similar to the distorted framework of $[Hg_7As_4](AgI_3)_2$ (Fig. 13 *c*). The deviations of the As—Hg—As angles from 180° lead to the formation of two types of cavities. The pyramidal $(SnI_3)^-$ anions, the geometry of which is determined by Gillespie's rules, are arranged in a chess-like fashion and occupy one-half of the framework cavities. The anion is fixed within the framework cavity through weak electrostatic interactions, four interactions per iodine atom of the anion at distances of ~3.4 Å to the framework mercury atoms (Fig. 13 *f*). The second half of the cavities are occupied by additional iodine atoms, three atoms per cavity. These iodine atoms can be considered either as a part of the framework or as guest anions, because the Hg—I distances are in the range of 3.16–3.23 Å (see Fig. 13 *e*), which correspond to strong interactions with the framework and are only slightly longer than the typical covalent bond distances between the mercury and iodine atoms. Therefore, the formula of the compound can be written as $[Hg_7As_4I_3](SnI_3)$ or $[Hg_7As_4](I)_3(SnI_3)$.

The simultaneous decrease in the sizes of the halogen and pnictogen atoms can give rise to the isostructural compound $[Hg_7P_4Br_3](SnBr_3)$.[31] The replacement of the bitetrahedral Hg_7Z_2 unit in the $[Hg_7Z_4]^{4+}$ framework by the octahedral Hg_6Z_2 unit leads to a decrease in the size of the framework cavities, thus making it possible to trap smaller anions, like in the compounds described in Section 2.2. Five compounds of this type containing trigonal-pyramidal guest anions are known — $[Hg_6P_4Cl_3](SnCl_3)$, $[Hg_6As_4Cl_3](SnCl_3)Hg_{0.13}$, $[Hg_6As_4Br_3](SnBr_3)$, $[Hg_6Sb_4I_3]$. $.(SnI_3)Hg_{0.16}$ (Ref. 31) and $[Hg_6P_4Cl_3](PbCl_3)$ [21] (Fig. 14). The frameworks of these complexes built up from octahedral Hg_6Z_2 structural units contain additional halogen atoms and, at the same time, they are structurally similar to the '64' framework (see above) and have two types of closed cavities. The large cavities in the $[Hg_6Z_4X_3]^+$ frameworks are occupied by guest $(MX_3)^-$ anions. The pyramidal $(SnX_3)^-$ anion adopts similar coordination geometry in two types of frameworks ($[Hg_7Z_4X_3]^+$ and $[Hg_6Z_4X_3]^+$). Thus, each halogen atom is coordinated by four mercury atoms at distances up to 4 Å (see Figs. 13 *f* and 14 *c*). Additional

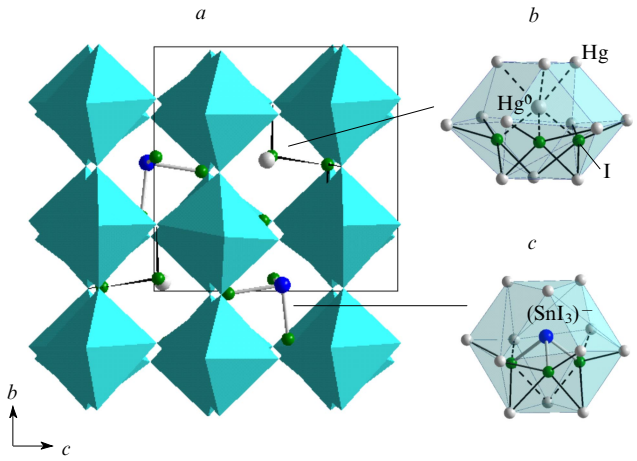


Figure 14. Crystal structure of $[Hg_6Sb_4I_3](SnI_3)Hg_{0.16}$. The data for the figure were taken from Ref. 31.
(*a*) Overall view; filling of the cavities in the frameworks formed by mercury atoms: (*b*) small cavities filled by mercury and iodine atoms; (*c*) large cavities filled by $(SnI_3)^-$ anions (black lines indicate the distances < 4 Å).

halogen atoms occupy small framework cavities and are linked to the octahedral units in such a way that each mercury atom is linked to halogen (see Fig. 14 *b*). The Hg–X distances for the framework halogen atom are smaller that the corresponding distances in the compounds $[Hg_7As_4I_3](SnI_3)$ and $[Hg_7As_4Br_3](SnBr_3)$ (see Table 2). The remaining space in the small framework cavities can be filled with Hg^0 atoms, as exemplified by the compound $[Hg_6Sb_4I_3](SnI_3)Hg_{0.16}$ in Fig. 14 *b*.

The host framework has a substantial effect on the geometry of tin-containing guest anions. Quantum chemical calculations [39] demonstrated that the geometry of the $(SnX_3)^-$ anions in the crystal structures of all compounds substantially differs from the calculated equilibrium value. In all crystal structures, the Sn–X bond lengths are larger and the X–Sn–X bond angles are smaller than the corresponding equilibrium values. A comparison of the observed geometry of the same guest anion in different crystal structures with the calculated equilibrium geometry showed that the same guest anion is much more distorted in $[Hg_6As_4Br_3](SnBr_3)$ than in $[Hg_7P_4Br_3](SnBr_3)$ and in $[Hg_6Sb_4I_3](SnI_3)Hg_{0.16}$ than in $[Hg_7As_4I_3](SnI_3)$. These differences are quite understandable. The positive charge of the cationic host framework is distributed over the inner surface of the cavity. In the structures of $[Hg_7P_4Br_3](SnBr_3)$ and $[Hg_7As_4I_3](SnI_3)$, the size of the cavity occupied by the guest anion is larger due to the presence of an additional mercury atom. Consequently, the charge per cavity is smaller compared to all other cases, and electrostatic interactions between the guest and the $[Hg_7Z_4X_3]^+$ host framework in these compounds are weaker. Weaker host–guest interactions lead to smaller deviations of the geometry of the $(SnX_3)^-$ anion from equilibrium values. A comparison of the crystal structures of $[Hg_6P_4Cl_3](SnCl_3)$ and $[Hg_6As_4Cl_3](SnCl_3)$ demonstrated that their frameworks are structurally similar Although the cavities within these frameworks have different sizes, the deviation of the geometry of the $(SnCl_3)^-$ anion from equilibrium values is nearly equal in both structures.

In this case, it is these weak electrostatic interactions that control the geometry of the guest $(SnX_3)^-$ anion and the type of the resulting host framework provided that the requirements of geometric compatibility between the host cavity and the guest size are modest.

4. Complex anions and frameworks

If a metal atom involved in the guest is prone to form various halometallate anions, the type of the resulting compound substantially depends on the conditions of synthesis. The compound $[Hg_6As_4](BiCl_6)Cl$,[55] which contains the octahedral $(BiCl_6)^{3-}$ anion as a guest in the cavities of the $[Hg_6As_4]^{4+}$ framework, or the compound $[Hg_8As_4](Bi_3Cl_{13})$,[36] which contains the complex polymeric $^1_\infty(Bi_3Cl_{13})^{4-}$ anion in the channels of the new type of the framework, can be prepared in the Hg–As–Bi–Cl system by varying the composition of the starting components, as well as the time and temperature of the synthesis. The framework in the crystal structure of $[Hg_8As_4](Bi_3Cl_{13})$ is built up only from mercury atoms linearly coordinated by pnictogen atoms and, correspondingly, pnictogen atoms tetrahedrally coordinated only by mercury atoms. The Hg_4Z tetrahedra are connected *via* sharing all vertices to form a three-dimensional honeycomb-like $[Hg_8As_4]^{4+}$ framework. The structure of the latter can be described as cylinders linked to each other by mercury and pnictogen atoms with a one-dimensional helical-like tunnel along the *c* axis (Fig. 15 *a*). The cylinders are formed by two concentric Hg–Z helices bridged by mercury atoms *via* Hg–Z bonds. Infinite helical $^1_\infty(Bi_3Cl_{13})^{4-}$ chains are embedded in the tunnels of the $[Hg_8As_4]^{4+}$ framework (Fig. 15 *b*). This anion is composed of distorted $BiCl_6$ octahedra and $BiCl_7$ pentagonal bipyramids in a ratio of 2 : 1, which are linked by sharing faces. The framework of the compound $[Hg_8As_4](Bi_3Cl_{13})$ can be described by a minimum repeating unit $[Hg_6As_3]^{3+}$, but the ratio of $[Hg_6As_3]^{3+}$ to $^1_\infty(Bi_3Cl_{13})^{4-}$ should be 4 : 3 to achieve charge balance between host and guest.

The compound $[Hg_6P_3](In_2Cl_9)$ [36] is assembled under the same conditions as $[Hg_8As_4](Bi_3Cl_{13})$. The frameworks of these compounds are structurally similar. The tunnels of the $[Hg_6P_3]^{3+}$ framework capture guest $(In_2Cl_9)^{3-}$ anions, which are composed of two distorted face-sharing $InCl_6$ octahedra and are located around a helical axis (Fig. 15 *c*).

The framework, which is unknown for other anions, is assembled about the discrete dinuclear guest $(Bi_2Br_{10})^{4-}$ anion. The compound with the general formula $[Hg_7(HgBr)_2As_4]. .(Bi_2Br_{10})$ [37] was synthesized by prolonged heating of a mixture of the starting compounds. The positively charged $[Hg_7(HgBr)_2As_4]^{4+}$ framework (Fig. 16) was built up from Hg_4As tetrahedra, half of which share all vertices, while the other half share only three of the four vertices. All mercury atoms have nearly linear coordination geometry: seven of the nine mercury atoms are linked only to two arsenic atoms, and two mercury atoms are linked to one arsenic atom and one bromine atom. Therefore, the $[Hg_7(HgBr)_2As_4]^{4+}$ framework contains additional halogen atoms, which supplement the coordination of the bismuth atom of the guest anion. The $(Bi_2Br_{10})^{4-}$ anion can be considered as a unit composed of two vertex-sharing $BiBr_6$ octahedra.[68] One of the octahedra is almost undistorted. The other one is better described as a tetragonal pyramid with a bismuth atom in the base, because one of bromine

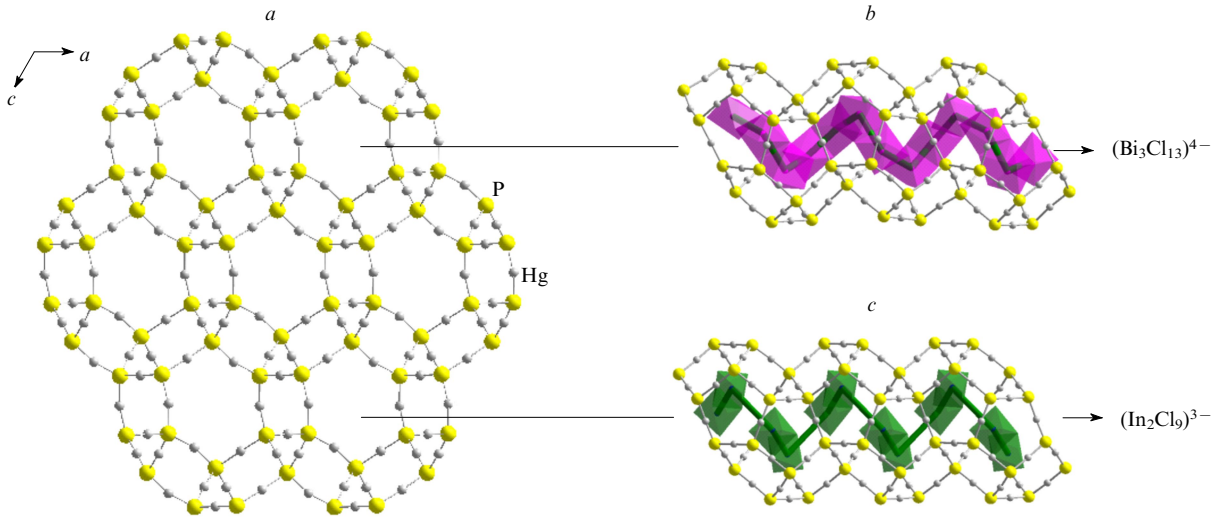


Figure 15. Idealized representation of the framework of the compounds $[Hg_8As_4](Bi_3Cl_{13})$ and $[Hg_6P_3](In_2Cl_9)$ projected onto the *ac* plane (*a*); the arrangement of $_{\infty}^{1}(Bi_3Cl_{13})^{4-}$ (*b*) and $(In_2Cl_9)^{3-}$ anions (*c*) in the tunnels running along the *b* axis. The data for the figure were taken from Ref. 36.

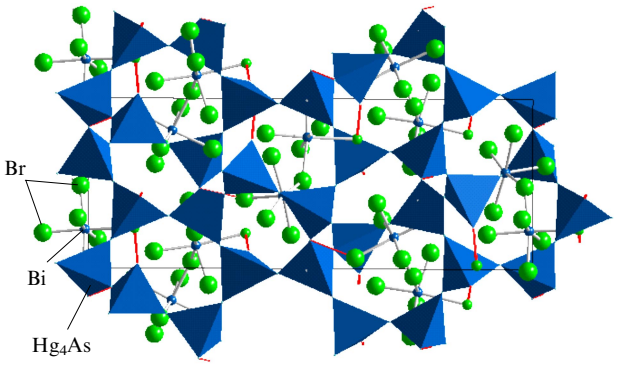


Figure 16. Overall view of the crystal structure of $[Hg_7(HgBr)_2As_4](Bi_2Br_{10})$. The data for the figure were taken from Ref. 37.
The bonds between the framework formed by Hg_4As tetrahedra (blue) and bromine atoms shared by the framework and the guest anion are indicated by red lines.

atoms is located at a rather large distance (3.26 Å) and is a terminal framework atom.

5. Change of the coordination site. Cadmium compounds

In the presence of sufficient amounts of mercury atoms, cadmium, which is not prone to be coordinated in a linear fashion, tends to be involved in the guest anion rather than in the framework. In the compounds $[Hg_6As_4](CdBr_6)$, $[Hg_6As_4](CdCl_6)Hg_{0.4}$, $[Hg_6Sb_4](CdI_6)Hg_{0.6}$,[48] cadmium occupies the position at the centre of the octahedral guest. Since the Z–Hg–Z angles in '64' frameworks deviate from linear geometry, cadmium occupies the mercury position in the framework, if mercury atoms are absent, to form the complex $[Cd_6P_4](CdCl_6)$,[69, 70] isostructural with compounds $[Hg_6Z_4](M^{2+}X_6)$.

In tridymite-like $[Hg_2Z]^+$ frameworks, the Z–Hg–Z angles are close to 180°. Therefore, it is of interest to compare the crystal structures of $[Hg_2P]_2(HgBr_4)$[11] and $[Cd_2P]_2(CdBr_4)$.[17] These compounds differ only by the nature of the Group 12 atom; however, this difference leads to topologically different frameworks (Fig. 17). Mercury is easily adapted to the linear coordination environment by two phosphorus atoms, whereas cadmium prefers the tetrahedral coordination. As a consequence, despite the fact that both frameworks retain the tridymite-like topology, the geometry of the framework in the compound $[Cd_2P]_2(CdBr_4)$ is highly distorted, and the P–Cd–P angles substantially deviate from 180° (vary from 146 to 166°).

6. Complex linkers

The structure of a metal-inorganic framework can be varied not only by combining Hg_4Z, Hg_6Z_2 and Hg_2, Hg_3 structural units (see the upper part of Fig. 18) but also by complicating the linkers. The frameworks considered above contain discrete Z^{3-} anions and(or) $(Z_2)^{4-}$ dumbbells as linkers. More complex linkers (see Fig. 18 *a–d*) have as yet been found only in a few mercury pnictide halides and in Hg–Ag–P–X systems (X = Cl, Br, I), because only a limited number of studies have addressed this issue.

6.1. Compounds M_2Z_3X with $_{\infty}^{1}[Z]^-$ chains

The structures of mercury and cadmium pnictide halides with the general formula M_2Z_3X (M = Hg, Cd; Z = P, As; X = Cl, Br, I) contain infinite chains of pnictogen atoms.[71, 76, 77] Zigzag six-step $_{\infty}^{1}[Z]^-$ chains are chiral and are twisted around the *c* axis. In some M_2Z_3X compounds, the chains have the same chirality, while in the other, chains of opposite chirality alternate in a ratio of 1 : 1. Each pnictogen atom has a distorted tetrahedral coordination environment formed by two pnictogen atoms and two mercury or cadmium atoms (Fig. 19 *b*), which act as bridges between adjacent chains, thus forming the $[M_2Z_3]^+$ framework. Halogen atoms are located in the channels running along the *c* axis. In all cases, the distances from these atoms to the framework mercury atoms are somewhat shorter than the Hg–X distance corresponding to the second coordina-

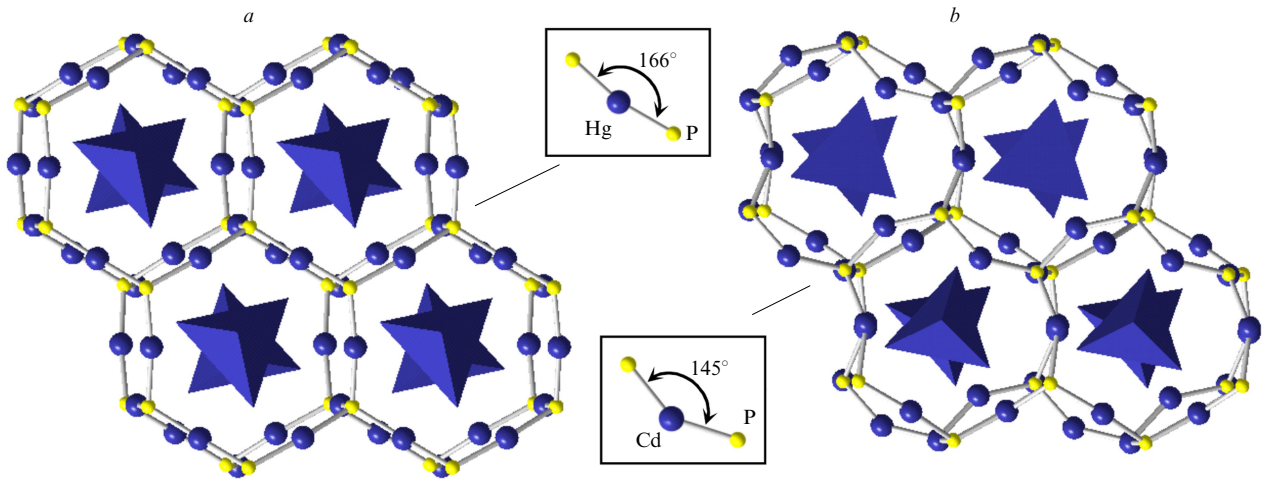


Figure 17. The crystal structures of $[Hg_2P]_2HgBr_4$ (*a*) and $[Cd_2P]_2CdBr_4$ (*b*). The data for the figure were taken from Ref. 11 (*a*) and Ref. 17 (*b*).

tion sphere (Fig. 19 *a*,*c*). All M_2Z_3X compounds, except for the mercury arsenide bromide Hg_2As_3Br, are semiconductors. The latter one exhibits metallic conductivity, which is attributed to the overlap of the filled conduction band and the empty valence band and the appearance of Hg–Hg bonding interactions at the bottom of the conduction band.

6.2. Compounds with two coordination centres

6.2.1. Compounds $[Hg_7Ag_2P_8]Br_6/I_6$ and $[Hg_6Ag_4P_8]Br_6$. The $(P_6)^{6-}$ clusters

The isostructural compounds $Hg_7Ag_2P_8Br_6$ and $Hg_7Ag_2P_8I_6$ were synthesized.[72] The frameworks of these compounds contain silver atoms along with mercury. Their crystal structures have a three-dimensional positively charged framework built up from mercury and silver atoms and phosphorus clusters in the form of dumbbells and chair-like six-membered rings (see Fig. 18 *a*). All phosphorus atoms have a slightly distorted tetrahedral coordination environment. Taking into account the number of homonuclear bonds formed by the phosphorus atoms, the observed phosphorus moieties can be written as $(P_2)^{4-}$ and $(P_6)^{6-}$. The mercury and silver atoms linearly coordinated by phosphorus atoms occupy different positions. The Hg–P distances substantially differ from the Ag–P distances. The mercury atoms are arranged in an octahedron around the $(P_2)^{4-}$ dumbbell. In the *ab* plane, the $(P_6)^{6-}$ clusters are linked to silver atoms; in the *bc* plane, these clusters are further bridged to Hg_6P_2 octahedra by mercury atoms along the *c* axis (Fig. 20 *b*). The resulting three-dimensional $[(Hg_6^{2+}P_2)^{8+}Ag_2^{+}Hg^{2+}P_6^{6-}]^{6+}$ framework traps six halide anions in the cavities, thus ensuring the electroneutrality of the compound. In the framework cavities, halogen atoms bearing a formal charge of 1– are located at distances of 3 Å from the metal atoms of the $[Hg_7Ag_2P_8]^{6+}$ framework. The formula of the compound can be written as $[Hg_7Ag_2P_8]X_6$.

The results of band structure calculations for the compounds $Hg_7Ag_2P_8X_6$ (X = Br, I) are somewhat inconsistent with the ionic model proposed above for these complexes because the filled levels of the anion lie higher in energy than most of filled levels of the framework. The halogen p-orbitals make the major contribution to the states lying immediately below the Fermi level. The band gap width decreases from 1.0 to 0.8 eV on going from bromide to iodide, which is in good agreement with an increase in the energy of iodine p-orbitals compared to the corresponding

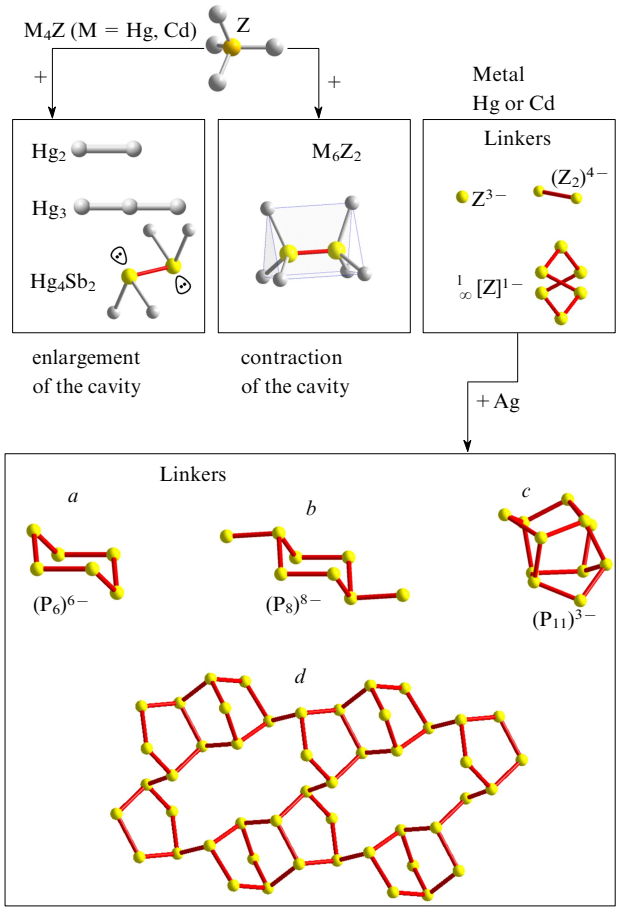


Figure 18. Structural units in mercury–pnictogen frameworks. (*a*–*d*) See the text. The data for the figure were taken from Refs 5, 23, 25, 51, 71–75.

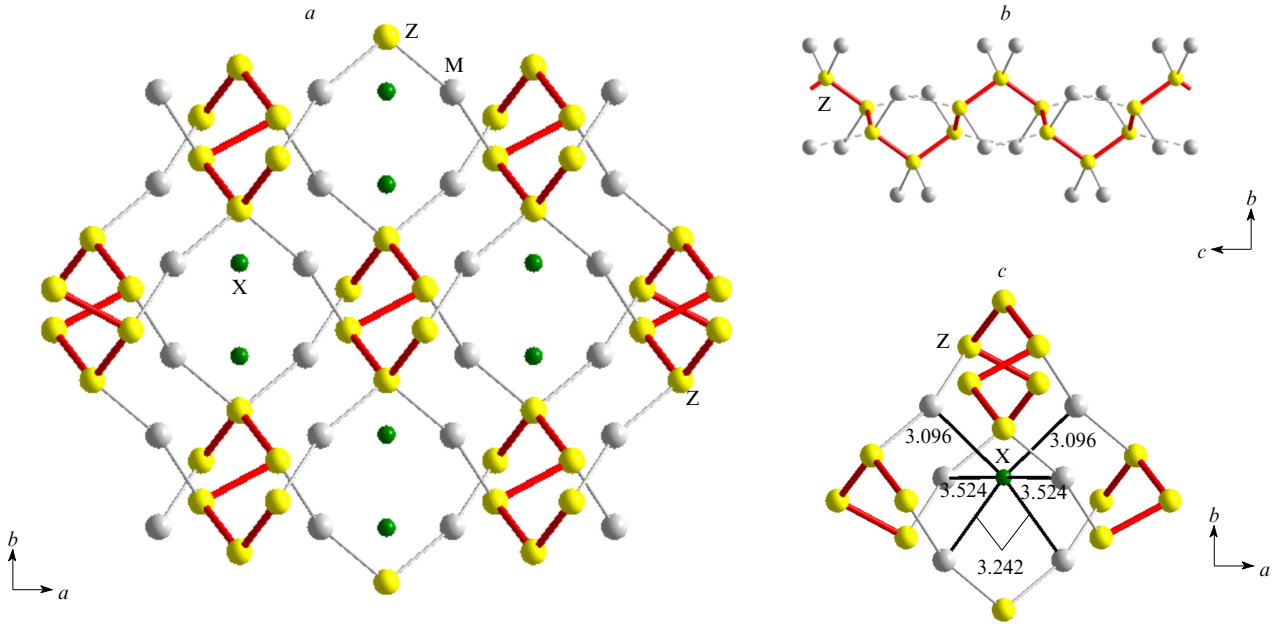


Figure 19. Overall view of the crystal structure of M_2Z_3X (M = Hg, Cd; Z = P, As; X = Cl, Br, I) (*a*), the $_{\infty}^{1}[Z]^{-}$ polymeric chain (*b*) and the guest X^{-} anion in the compound Hg_2As_3Br (*c*). The data for the figure were taken from Refs 71 and 77.
(*b*) Solid lines indicate the basic coordination environment of pnictogen atoms; dashed lines indicate bonds with atoms that complete the coordination environment at larger distances.

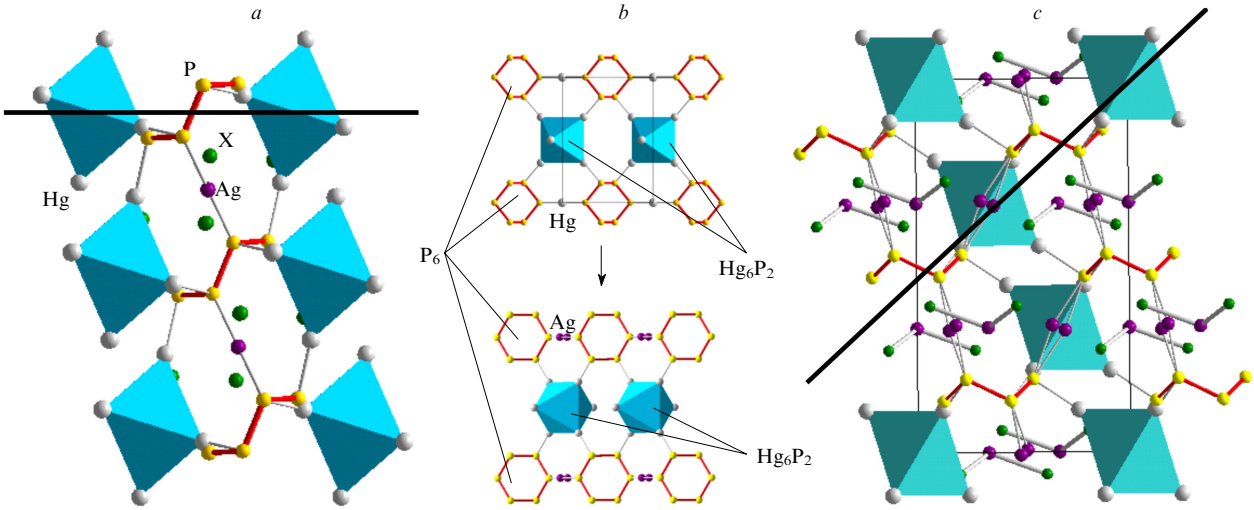


Figure 20. Overall view of the crystal structures of $[Hg_7Ag_2P_8]X_6$ (X = Br, I) (*a*) and $[Hg_6Ag_3P_8](AgBr_3)Br_3$ (*c*) projected onto the *ac* plane and the transformation from the $[Hg_7Ag_2P_8]^{6+}$ framework to the $[Hg_6Ag_3P_8]^{5+}$ framework upon replacement of mercury by silver (*b*). Thick lines indicate the planes that contain layers of P_6 clusters. The data for the figure were taken from Ref. 72.

bromine orbitals. Analysis of the orbital contribution to the density of states demonstrated that host–guest interactions, such as Hg···Br and Ag···Br, are relatively weak and diffuse, while Ag–P interactions and particularly Hg–P interactions within the host framework are very strong and directional. Therefore, it can be argued that numerous weak M–Br interactions (M = Ag, Hg) determine the definite arrangement of guest halide anions in the tunnels of the host framework.

The compound $[Hg_6Ag_4P_8]Br_6$ was synthesized at higher temperature.[72] This compound is not isostructural with the above-described compounds $[Hg_7Ag_2P_8]X_6$ (X = Br, I); however, their frameworks are structurally very similar (Fig. 20 *c*). The difference is that the mercury atom, which is not included in the octahedral Hg_6P_2 unit in the $[(Hg_6^{2+}P_2)^{8+}Ag_2^{+}Hg^{2+}P_6^{6-}]^{6+}$ framework of the compound $[Hg_7Ag_2P_8]Br_6$, is replaced by silver giving rise to the $[(Hg_6^{2+}P_2)^{8+}Ag_3^{+}P_6^{6-}]^{5+}$ framework (Fig. 20 *b*). In this structure, one pyramidal $(AgBr_3)^{2-}$ anion is present instead of

half of bromide ions to ensure the electroneutrailiy of the compound as a whole. The formula of the compound can be written as $[Hg_6Ag_3P_8](AgBr_3)Br_3$.

6.2.2. Compound $[Hg_4Ag_5P_8](AgCl_4)Cl$. The $(P_8)^{8-}$ clusters

The compound $[Hg_4Ag_5P_8]Cl_5$ containing the previously unknown phosphorus cluster $(P_8)^{8-}$ was synthesized using a higher Ag : Hg ratio.[73] This phosphorus cluster is a six-membered ring adopting a chair conformation with two terminal phosphorus atoms in *para* positions (see Fig. 18 *b*). The $(P_8)^{8-}$ clusters are packed in layers in the *ab* plane. In the layer, the clusters are arranged in a staggered fashion and are linked together by mercury atoms, the free space in the layer being occupied by chlorine atoms (Fig. 21 *a*). This motif can be represented as $\{Hg_2P_8Cl\}$. The structure of the layer can also be considered as derived from the two-dimensional corrugated layer of grey arsenic, in which homonuclear bonds are partially broken by mercury and chlorine atoms. These layers alternate with $\{Ag_5Cl_4\}$ layers along the *c* axis of the unit cell. In the $\{Ag_5Cl_4\}$ layers, there are shorter (2.72 Å) and longer (2.85 Å) Ag–Cl distances (in Fig. 21 *b*, these distances are indicated by solid and dashed lines, respectively). Both values are similar to the corresponding distances in silver chloride.[78] Meanwhile, the silver atoms located at larger distances from chlorine atoms act as bridges between the $\{Hg_2P_8Cl\}$ and $\{Ag_5Cl_4\}$ layers, resulting in the formation of a three-dimensional framework (Fig. 21 *a*–*c*), and form bonds with phosphorus atoms. All phosphorus atoms adopt a weakly distorted tetrahedral coordination geometry. However, these atoms are in different formal oxidation states. Each terminal phosphorus atom forms a homonuclear bond and is linked to three metal atoms (Ag + 2 Hg). Consequently, according to the Zintl–Klemm concept, the formal oxidation state of these atoms is 2–. Four atoms belonging to the six-membered ring are linked to two other phosphorus atoms and two metal atoms (Ag + Hg). Therefore, the formal charge on each phosphorus atom is 1–. The remaining two atoms of the six-membered ring each form three homonuclear bonds. Since the terminal phosphorus atoms are linked to these two atoms, the coordination environment of the latter is completed by one silver atom. Therefore, these atoms are formally uncharged. The formula of the compound can be written as $[Hg_4Ag_4P_8](AgCl_4)Cl$. It exists in two polymorphs, which differ in the packing mode of the $(P_8)^{8-}$ layers in the crystal structures.

Based on the results of band structure calculations for the ordered monoclinic modification performed by the density functional theory in the linear muffin-tin orbital atomic-sphere approximation, it was shown[73] that the oxidation states formally assigned to the phosphorus atoms do not occur; however, the charge distribution pattern in correct. Thus, the phosphorus atom in the ring that is involved in three mononuclear bonds bears a negative charge, whereas the terminal phosphorus atom, on the contrary, has the highest negative charge. Analysis of orbital interactions demonstrated that the M–P bond is a result of overlap of phosphorus p-orbitals with mercury s- and p-orbitals and silver d- and s-orbitals. The chlorine p-orbitals and silver d-orbitals make the major contribution to the band lying immediately below the Fermi level. Therefore, the orbitals of the $(P_8)^{8-}$ polyanion have a minor

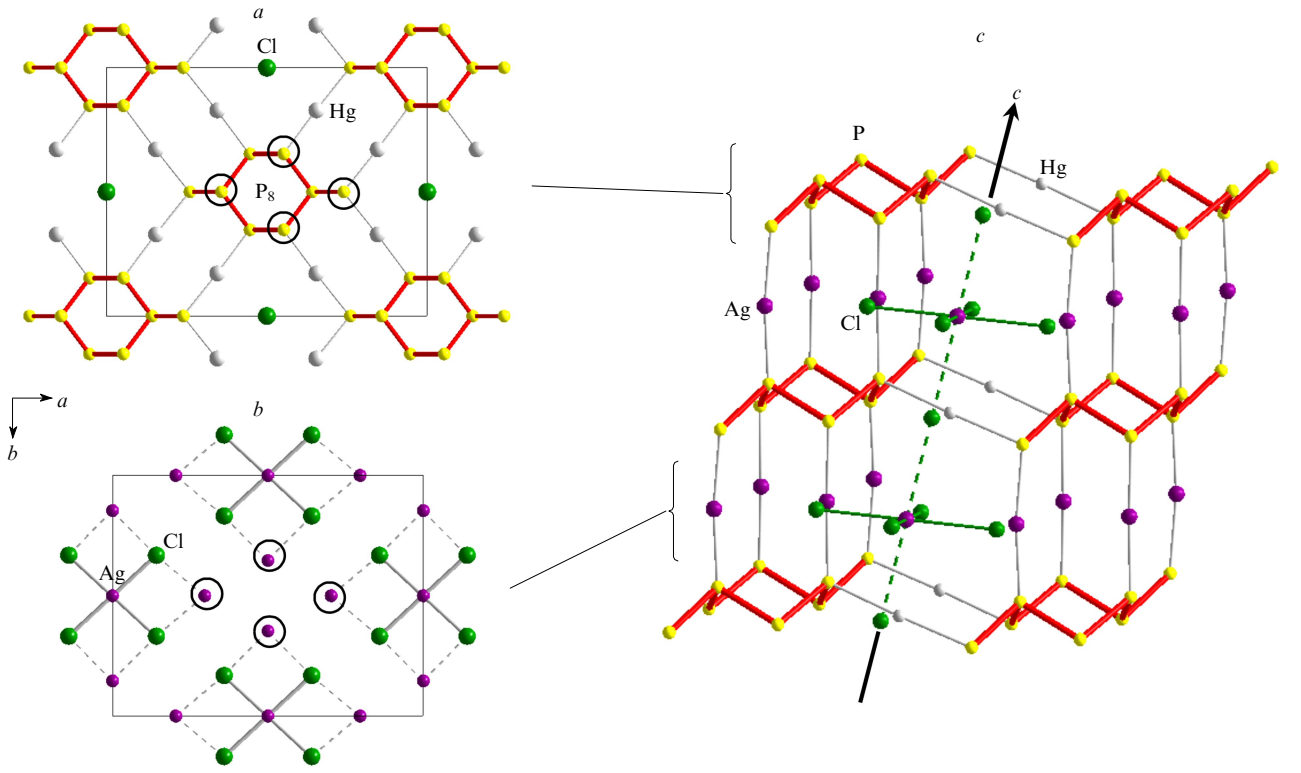


Figure 21. The $\{Hg_2P_8Cl\}$ (*a*) and $\{Ag_5Cl_4\}$ layers (*b*) projected onto the *ab* plane and the crystal structure of $[Hg_4Ag_4P_8](AgCl_4)Cl$ projected along the *c* axis (*c*). The data for the figure were taken from Ref. 73.
The atoms acting as bridges between the layers are encircled.

impact on the electrical properties of the compound (the band gap width is 1.0 eV).

6.2.3. Compound $Hg_{12}Ag_{41}P_{88}I_{41}$. The $(P_{11})^{3-}$ clusters

Compounds having mercury–pnictogen frameworks are rather sensitive to the conditions of synthesis. Hence, compounds with different compositions and structures can be synthesized under appropriate conditions. Apart from $[Hg_7Ag_2P_8]I_6$, two compounds — $Hg_{12}Ag_{41}P_{88}I_{41}$ (Ref. 74) and $HgAg_6P_{20}I_2$ (Ref. 75) — can form in the Hg–Ag–P–I system.

The distinguishing feature of the crystal structure of $Hg_{12}Ag_{41}P_{88}I_{41}$ is the presence of cage anionic $(P_{11})^{3-}$ clusters composed of eight three-connected (P^0) and three two-connected (P^-) phosphorus atoms (see Fig. 18 *c*). The structure of these clusters can be considered as derived from the as-yet unknown phosphocubane molecule, which has six pentagonal faces instead of the initial square faces due to the presence of three bridging phosphorus atoms. Earlier, $(P_{11})^{3-}$ anions were found only in ionic compounds, *e.g.*, in M_3P_{11} (M = Na, K, Rb, Cs).[79–81] In the compound $Hg_{12}Ag_{41}P_{88}I_{41}$, these anions (the first case) form a covalently bonded structure. Within 1/8 of the unit cell (octant), the arrangement of $(P_{11})^{3-}$ anions is similar to that of the sulfur atoms in the sphalerite structure. The anions are linked to each other by silver atoms, which are connected to the phosphorus atoms in the formal oxidation sate 0, and the clusters of adjacent octants are bridged by mercury atoms that are linked to the phosphorus atoms in the oxidation state 1– (Fig. 22 *a*). The mutual arrangement of octants is such that the geometric centres of $(P_{11})^{3-}$ clusters form two types of polyhedra — a cube and a rhombicuboctahedron linked by sharing common square faces (Fig. 22 *b*). In the compound $Hg_{12}Ag_{41}P_{88}I_{41}$, the larger rhombicuboctahedron traps iodine and silver atoms, which form a $(2\times2\times2)$ α-AgI-type unit. Iodine atoms in this structural unit are arranged in a body-centred cube fashion, while silver atoms are randomly distributed between the iodine atoms. An octahedron formed by iodine atoms is located inside the cube of $(P_{11})^{3-}$ clusters, with several disordered silver positions at the centre of the latter. This can also be considered as a part of the α-AgI structure (Fig. 22 *b*).

6.2.4. Compound $HgAg_6P_{20}I_2$. The $^1_\infty(P_{10})^{3-}$ ribbon

The compound $HgAg_6P_{20}I_2$ was produced as an impurity in the synthesis of $Hg_{12}Ag_{41}P_{88}I_{41}$. The previously unknown phosphorus polyanion $^1_\infty(P_{10})^{3-}$ (see Fig. 18,*d*) found in the crystal structure of $HgAg_6P_{20}I_2$ has a unique structure. This anion is composed of tubular P_{10} units similar to those in silver polyphosphide Ag_3P_{11}.[82] As opposed to the phosphide Ag_3P_{11}, in which the tubular moieties are linked together to form layers, the tubular moieties in the new compound form one-dimensional infinite ribbon-like polyanions. In the crystal structure of $HgAg_6P_{20}I_2$, the $^1_\infty(P_{10})^{3-}$ polyanions are bridged by mercury and silver atoms (Fig. 23 *a*). In this structure, the mercury atoms are linked only to phosphorus atoms in the formal oxidation state 1–, and the silver atoms are connected to two types of phosphorus atoms bearing the formal charges 1– and 0. Therefore, phosphorus atoms in different oxidation states in this compound are also preferentially bound to different cations. The mercury and silver coordination polyhedra can be described as more or less distorted tetrahedra formed by phosphorus and iodine atoms. The iodine atoms are located between $^1_\infty(P_{10})^{3-}$ polyanions in the direction perpendicular to the *ab* plane and occupy two independent crystallographic positions because they are in different coordination environments — either tetrahedral formed by one mercury atom and three silver atoms or angular formed by silver and mercury atoms (Fig. 23 *b*).

In the case of the simultaneous involvement of mercury and silver atoms in the formation of the framework, the charge of the latter should be lower; however, instead, the phosphorus atoms are involved in homonuclear bonds giving rise to clusters or extended structures.

Phosphorus linkers become more complex with an increase in the Ag : Hg ratio. Both types of framework metal atoms have a very similar nearly linear coordination geometry. A decrease in the charge of the cation on going

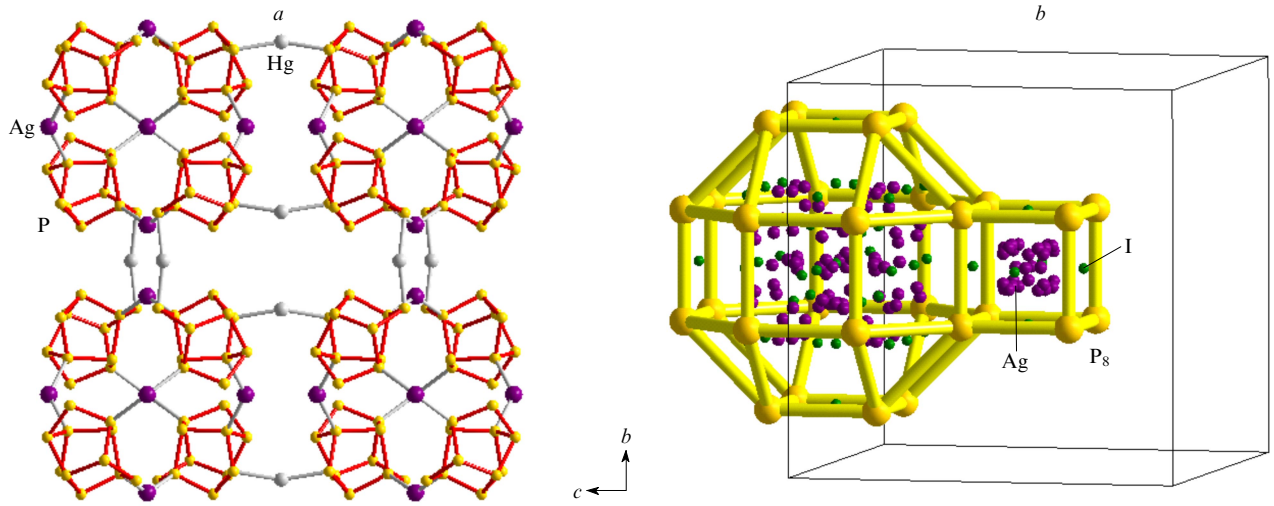


Figure 22. Connection of $(P_{11})^{3-}$ clusters in the unit cell of the crystal structure of $Hg_{12}Ag_{41}P_{88}I_{41}$ (*a*) and the distribution of α-AgI units in polyhedra formed by $(P_{11})^{3-}$ clusters (*b*). The data for the figure were taken from Ref. 74.

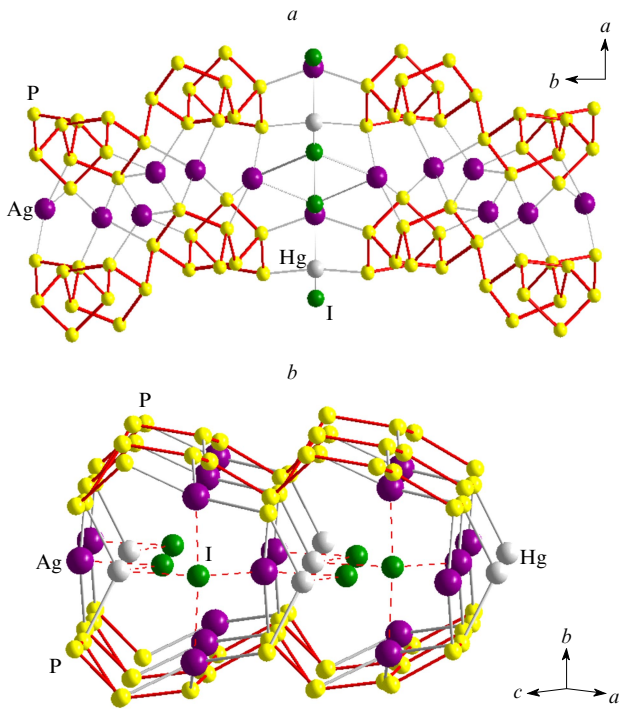


Figure 23. Overall view of the crystal structure of $HgAg_6P_{20}I_2$ projected onto the *ab* plane (*a*) and the coordination environment of iodine atoms located in the channels running along the *ac* diagonal (*b*).
Dashed lines indicate the shortest distances. The data for the figure were taken from Ref. 75.

from Hg^{2+} to Ag^{+} leads to an increase in the average oxidation state of pnictogen in these compounds. The lower the Hg : Ag ratio, the higher the average formal oxidation state of phosphorus in the compound. Another important conclusion can be drawn from analyzing the environment of the phosphorus clusters by Hg^{2+} and Ag^{+} cations. Thus, the phosphorus atoms in the highest negative oxidation state are preferentially bound to mercury atoms, while the phosphorus atoms bearing the smallest negative charge are preferentially connected to silver atoms, which also accounts for the separation of mercury and silver in positions of the crystal structures. A change in the Ag : Hg ratio will require the change in both the charge and the number of anions in the structures.

7. Conclusion

The compounds considered in the review belong to a large family which can be described as metal-inorganic frameworks. The main principle of their crystal structures is a combination of positively charged covalently bonded frameworks and guest anions that occupy the framework cavities. The frameworks are based on linearly (rarely, tetrahedrally) coordinated 11 – 12 Group metal atoms, which are linked together by four-connected Group 15 elements to form three-dimensional systems. The four-connectivity exists in different systems, from simple Z^{3-} anions surrounded by four metal atoms to complex clusters and one-dimensional infinite structures. Anionic guests of different nature occupy framework cavities, the host – guest complementarity in terms of charge, geometry and topology being maintained.

Compounds of this type demonstrate the ranges of possible incompatibility between host and guest, as well as of their mutual adjustment to ensure complementarity. Relative flexibility of the subsystems is determined by specific features of chemical bonding — the covalency of the framework and the guest anion and a weak electrostatic (sometimes van der Walls) character of host – guest interactions.

A comparison of this family of compounds and their organic counterparts clearly shows that inorganic derivatives are scarce. Hence, these compounds are not widely used. There are sparse data in the literature concerning the potential use of phases with mercury – pnictogen frameworks as IR-transparent and luminescent materials. These compounds are also of interest as topological insulators. Evidently, metal-inorganic frameworks based on mercury or cadmium atoms are not attractive for application. However, a knowledge of the general principles of constructing these compounds will allow researchers to synthesize and characterize a large range of new toxic-free metal-inorganic frameworks in the near future. Hence, it can be expected that these compounds will attract more attention.

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