A New Family of Supramolecular Complexes with 3D Cationic Hg/Z Frameworks, SnX_3^- Guest Anions (Z = P, As, Sb; X = Cl, Br, I): Crystal Structures and Host−Guest Interactions

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Five new inorganic supramolecular complexes, $[Hg_6P_4Cl_3](SnCl_3)$ (**I**), $[Hg_6As_4Cl_3](SnCl_3)Hg_{0.13}$ (**II**), $[Hg_6As_4Br_3](SnBr_3)$ (**III**), $[Hg_6Sb_4I_3](SnI_3)Hg_{0.16}$ (**IV**), and $[Hg_7P_4Br_3](SnBr_3)$ (**V**), have been prepared and their structures determined by X-ray single crystal experiments. They all crystallize in the cubic space group $P2_13$ (No 198) with $Z = 4$, and unit cell parameters $a = 11.865(1)$ (**I**), 12.233(1) (**II**), 12.383(1) (**III**), 13.285(2) (**IV**), and 12.490(1) Å (**V**). The crystal structures of these compounds are composed of the 3D positively charged frameworks $[Hg_6Z_4X_3]^+$ (**I–IV**) or $[Hg_7P_4Br_3]^+$ (**V**), with SnX_3^- anions trapped in the larger cavities of the frameworks (X = Cl, Br, I; Z = P, As, Sb). In the structures of **II** and **IV** the smaller cavities are partly filled by mercury atoms. The structures of **I–V** and of previously reported $[Hg_7As_4I_3](SnI_3)$ (**VI**) are discussed with respect to the matching and mutual adjusting of the host frameworks and guest anions. A comparison of the observed and calculated (ab initio, RHF level) geometry of the SnX_3^- anions is used to analyze the weak host–guest interactions.

Introduction

Supramolecular inorganic compounds possess a huge variety of crystal structures and physical properties.[1] Among them a group of phases can be distinguished in which the three dimensional (3D) positively charged host framework is built up of linearly coordinated mercury and tetrahedrally coordinated pnicogen atoms.[2] Halometallate anions — guests of different shapes and sizes — reside in the cavities of the frameworks. These compounds may be exploited as convenient systems for the investigation of the role of the host-guest interactions in the formation and crystal structure organization of inorganic supramolecular architectures in which both host and guest fragments are electrically charged. For this purpose, a group of related phases with similar crystal structures should be used. In our previous work[2e] we reported on a novel supramolecular complex $[Hg_7As_4I_3](SnI_3)$ in which the cationic framework encapsulates the SnI_3^- anion. It therefore seemed obvious that different SnX_3^- anions (X = Cl, Br and I) may serve as templates for the formation of new Hg−Z (Z = P, As, Sb) cationic frameworks. We have performed a systematic search for such compounds, and here we report on the crystal structures of five new supramolecular phases: $[Hg_6P_4Cl_3](SnCl_3)$ (**I**), $[Hg_6As_4Cl_3](SnCl_3)Hg_{0.13}$ (**II**), $[Hg_6As_4Br_3](SnBr_3)$ (**III**), $[Hg_6Sb_4I_3](SnI_3)Hg_{0.16}$ (**IV**) and $[Hg_7P_4Br_3](SnBr_3)$ (**V**). The significant amounts of the materials isolated makes it possible to discuss the relationship between the structural organization of the title compounds and the host-guest complementarity.

Results and Discussion

The new compounds were obtained by a standard ampoule technique (see Exp. Sect. for details) exploiting the synthetic conditions previously reported for a similar compound.[2e] As a result of a systematic search for new phases in the Hg−Z−Sn−X systems performed in this and our previous[2e] work, six supramolecular compounds have been prepared (Table 1).

Table 1. Host-guest phases in the Hg−Z−Sn−X systems (cubic cell parameter a in Å, space group $P2_13$)

	Cl	Br	I
P	$[Hg_6P_4Cl_3](SnCl_3)$ (**I**), Type 1[a] $a = 11.865(1)$	$[Hg_7P_4Br_3](SnBr_3)$ (**V**), Type 2[b] $a = 12.490(1)$	not found
As	$[Hg_6As_4Cl_3](SnCl_3)Hg_{0.13}$ (**II**), Type 1 $a = 12.233(1)$	$[Hg_6As_4Br_3](SnBr_3)$ (**III**), Type 1 $a = 12.383(1)$	$[Hg_7As_4I_3](SnI_3)$ (**VI**), Type 2 $a = 13.110(1)$
Sb	not found	not found	$[Hg_6Sb_4I_3](SnI_3)Hg_{0.16}$ (**IV**), Type 1 $a = 13.285(2)$

[a] Type 1 framework: $[Hg_6Z_4X_3]^+$. [b] Type 2 framework: $[Hg_7Z_4X_3]^+$.

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The crystal structures of the five new phases prepared in this work were determined by means of single crystal X-ray diffraction (Table 2). Selected interatomic distances and bond angles are given in Table 3−7. All the reported compounds have a similar structural organization. Their crystal structures are composed of a 3D cationic host framework, built up of linearly coordinated mercury and tetrahedrally coordinated pnicogen atoms, and additional halogen atoms, and have two types of closed cavities of different sizes. The SnX_3^- guest anions are encapsulated in the larger cavities of the host framework (Figure 1). In all cases the separation between the halogen atoms of the guest anion and the mercury atoms of the host framework is much larger than the sum of the covalent radii of the respective elements — a feature that is characteristic of host-guest compounds. In the structures of **II** and **IV** the smaller cavities are partly filled by mercury atoms.

Despite the similarity of the reported compounds (the same $P2_13$ space group and the same type of guest anion) they possess two types of host frameworks with the general formulae $[Hg_6Z_4X_3]^+$ (**I−IV**) and $[Hg_7Z_4X_3]^+$ (**V**). The latter has the same structure as in the earlier reported compound $[Hg_7As_4I_3](SnI_3)$ (**VI**).[2e] The cationic framework of **V** contains two types of phosphorus atoms. While P(1) and P(2) are tetrahedrally coordinated by mercury atoms, P(3) and P(4) are joined into P_2^{4-} dumbbells, such that their nearest neighbors are one phosphorus and three mercury atoms. Compounds **I−IV** have frameworks of a different type, where all the pnicogen atoms are joined into Z_2^{4-} dumbbells. The structure of the host framework is closely related to that found in $[Hg_6As_4](HgBr_6)Hg_{0.4}$ [2b] and $[Hg_6As_4](M^{III}X_6)X$ (X = Cl, Br),[2f,2g] the only difference being that in the compounds reported here the additional halogen atoms modify the framework. The Hg−Z and Z−Z interatomic distances within the frameworks [d(Hg−P) = 2.37−2.45 Å; d(Hg−As) = 2.50−2.52 Å; d(Hg−Sb) = 2.67−2.69 Å; d(P−P) = 2.18 Å; d(As−As) 2.38−2.42 Å; d(Sb−Sb) = 2.76−2.80 Å] are in good agreement with those found in numerous mercury pnictide halides.[2,3]

Table 3. Selected interatomic distances and bond angles for **I**

Distances [Å]	
Sn−Cl(2)	2.615(10) ×3
P(1)−Hg(1)	2.447(6) ×3
P(2)−Hg(2)	2.436(6) ×3
P(3)−Hg(1)	2.443(7) ×3
P(4)−Hg(2)	2.424(6) ×3
P(1)−P(4)	2.18(2)
P(2)−P(3)	2.18(2)
Cl(1)−Hg(2)	2.814(11)
Cl(1)−Hg(1)	2.894(12)
Cl(2)−Hg(1)	2.947(9)
Cl(2)−Hg(2)	3.066(9)
Cl(2)−Hg(2)	3.177(9)
Cl(2)−Hg(2)	3.245(9)
Angles [°]	
Cl(2)−Sn−Cl(2)	86.5(3) ×3
P(3)−Hg(1)−P(1)	170.2(4)
P(4)−Hg(2)−P(2)	166.9(4)
P(4)−P(1)−Hg(1)	112.9(3) ×3
Hg(1)−P(1)−Hg(1)	105.9(4) ×3
P(3)−P(2)−Hg(2)	108.8(4) ×3
Hg(2)−P(2)−Hg(2)	110.1(4) ×3
P(2)−P(3)−Hg(1)	111.5(4) ×3
Hg(1)−P(3)−Hg(1)	107.3(4) ×3
P(1)−P(4)−Hg(2)	110.4(4) ×3
Hg(2)−P(4)−Hg(2)	108.5(4) ×3

The SnX_3^- anions residing in the larger cavities of the frameworks are formed by the unique tin and X(2) atoms and have the shape of a trigonal pyramid with the tin atom at the vertex. Such a geometry of the anions is in an agreement with the Gillespie−Nyholm rules:[4] the three halogen atoms and the lone electron pair of the Sn^{2+} cation form a pseudo-tetrahedron around the tin atom, the X−Sn−X angles being smaller than regular tetrahedral.

Table 2. Data collection and structure refinement parameters for **I−V**; space group $P2_13$, $Z = 4$, $\lambda = 0.71073$ (Mo-K_α)

	I	**II**	**III**	**IV**	**V**
Composition	$[Hg_6P_4Cl_3](SnCl_3)$	$[Hg_6As_4Cl_3](SnCl_3)Hg_{0.13(1)}$	$[Hg_6As_4Br_3](SnBr_3)$	$[Hg_6Sb_4I_3](SnI_3)Hg_{0.16(1)}$	$[Hg_7P_4Br_3](SnBr_3)$
a, Å	11.865(1)	12.233(1)	12.383(1)	13.285(2)	12.490(1)
V, Å^3	1670.3(2)	1830.6(3)	1898.8(3)	2344.7(6)	1948.4(3)
ρ (calcd.), Mg/m^3	6.596	6.751	7.351	7.373	7.248
μ, mm^{-1}	57.332	60.575	69.137	53.616	68.47
Theta range for data collection, deg.	2.43 to 27.96	2.35 to 26.98	2.33 to 25.98	2.17 to 25.97	2.31 to 27.87
Refl. collected/independ.	2302/771	2490/924	2330/870	2825/1052	2658/892
ref. parameters	54	57	53	57	56
R_1[a] $(F_0 > 4\sigma F_0)$	0.0620	0.0427	0.0553	0.0681	0.0560
wR_2[b] $(F_0 > 4\sigma F_0)$	0.1554	0.0916	0.1249	0.1424	0.1142
G-o-f on F^2	1.112	1.018	1.083	1.077	1.089
Largest diff. peak and hole, e Å^{-3}	5.256 and −4.282	1.702 and −1.724	3.197 and −2.508	3.522 and −2.764	6.084 and −5.145

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_0^2 - F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$, $w = [\sigma^2(F_0^2) + A\cdot p^2 + B\cdot p]^{-1}$; $p = (F_0^2 + 2F_c^2)/3$; A = 0.0150 (**I**), 0.0309 (**II**), 0.0217 (**III**), 0.0561 (**IV**), 0.0556(**V**); B = 0 (**I**, **II**, **IV**, **V**), 76.6 (**III**).

Table 4. Selected interatomic distances and bond angles for **II**

Distances [Å]	
Sn−Cl(2)	2.626(6) ×3
As(1)−Hg(2)	2.496(1) ×3
As(2)−Hg(1)	2.495(1) ×3
As(3)−Hg(2)	2.494(1) ×3
As(4)−Hg(1)	2.497(1) ×3
As(1)−As(4)	2.403(6)
As(2)−As(3)	2.378(6)
Hg(1)−Cl(2)	3.162(6)
Hg(1)−Cl(2)	3.275(6)
Hg(1)−Cl(2)	3.412(6)
Hg(2)−Cl(1)	2.943(7)
Hg(2)−Cl(2)	3.008(6)
Hg(3)−Cl(1)	3.11(1) ×3
Hg(3)−As(4)	3.25(1)
Hg(3)−Hg(1)	3.50(1) ×3
Hg(3)−Cl(2)	3.633(8) ×3
Angles [°]	
Cl(2)−Sn−Cl(2)	87.6(2) ×3
As(4)−As(1)−Hg(2)	109.2(1) ×3
Hg(2)−As(1)−Hg(2)	109.67(9) ×3
As(3)−As(2)−Hg(1)	109.0(1) ×3
Hg(1)−As(2)−Hg(1)	109.90(9) ×3
As(2)−As(3)−Hg(2)	110.55(9) ×3
Hg(2)−As(3)−Hg(2)	108.4(1) ×3
As(1)−As(4)−Hg(1)	106.1(1) ×3
Hg(1)−As(4)−Hg(1)	112.59(9) ×3
As(2)−Hg(1)−As(4)	163.0(1)
As(3)−Hg(2)−As(1)	166.5(1)

Table 5. Selected interatomic distances and bond angles for **III**

Distances [Å]	
Sn−Br(2)	2.771(5) ×3
As(1)−As(4)	2.395(9)
As(1)−Hg(2)	2.523(3) ×3
As(2)−As(3)	2.416(9)
As(2)−Hg(1)	2.522(3) ×3
As(3)−Hg(2)	2.523(3) ×3
As(4)−Hg(1)	2.522(3) ×3
Hg(1)−Br(1)	3.047(5)
Hg(2)−Br(1)	2.926(5)
Hg1−Br(2)	3.049(4)
Hg2−Br(2)	3.180(4)
Hg2−Br(2)	3.306(4)
Hg2−Br(2)	3.402(4)
Angles [°]	
Br(2)−Sn−Br(2)	87.47(18) ×3
Hg(2)−As(1)−Hg(2)	109.69(14) ×3
As(4)−As(1)−Hg(2)	109.26(15) ×3
As(3)−As(2)−Hg(1)	109.58(15) ×3
Hg(1)−As(2)−Hg(1)	109.36(15) ×3
As(2)−As(3)−Hg(2)	107.24(15) ×3
Hg(2)−As(3)−Hg(2)	111.60(13) ×3
As(1)−As(4)−Hg(1)	111.07(14) ×3
Hg(1)−As(4)−Hg(1)	107.82(14) ×3
As(4)−Hg(1)−As(2)	168.0(1)
As(1)−Hg(2)−As(3)	164.66(15)

Table 6. Selected interatomic distances and bond angles for **IV**

Distances [Å]	
Sn−I(2)	2.992(5) ×3
Sb(1)−Hg(2)	2.678(3) ×3
Sb(1)−Sb(4)	2.762(8)
Sb(2)−Hg(2)	2.685(3) ×3
Sb(2)−Sb(3)	2.796(9)
Sb(3)−Hg(1)	2.690(3) ×3
Sb(4)−Hg(1)	2.671(3) ×3
Hg(1)−I(1)	3.261(5)
Hg(2)−I(1)	3.056(4)
Hg(1)−I(2)	3.203(4)
Hg(2)−I(2)	3.402(4)
Hg(2)−I(2)	3.572(4)
Hg(3)−Sb(2)	3.22(5)
Hg(3)−I(1)	3.31(3) ×3
Hg(3)−Hg(2)	3.64(3) ×3
Hg(3)−I(2)	3.792(14) ×3
Angles [°]	
I(2)−Sn−I(2)	88.0(1) ×3
Hg(2)−Sb(1)−Hg(2)	113.12(11) ×3
Hg(2)−Sb(1)−Sb(4)	105.51(13) ×3
Hg(2)−Sb(2)−Hg(2)	113.96(11) ×3
Hg(2)−Sb(2)−Sb(3)	104.49(14) ×3
Hg(1)−Sb(3)−Hg(1)	111.69(13) ×3
Hg(1)−Sb(3)−Sb(2)	107.15(14) ×3
Hg(1)−Sb(4)−Hg(1)	108.65(13) ×3
Hg(1)−Sb(4)−Sb(1)	110.28(13) ×3
Sb(4)−Hg(1)−Sb(3)	165.41(17)
Sb(1)−Hg(2)−Sb(2)	158.96(15)

The interesting feature of **II** and **IV** is that the additional mercury atoms partly occupy small cavities of the host framework. The coordination sphere of such a guest consists of 10 neighbors [3X(1), 1Z, 3Hg, and 3X(2) atoms]. The high coordination number of these mercury atoms, together with the large distances in their first coordination sphere (3.11−3.79 Å), indicate their low oxidation state. Mercury atoms serving as clathrated guests have already been observed in $[Hg_6As_4](HgCl_6)Hg_{0.4}$ [2a] where a zero oxidation state of the guest mercury was confirmed by means of solid state ^{199}Hg NMR spectroscopy.[5] It is not yet clear what factors control the population of mercury atoms in the smaller cavities of different frameworks. The results of this research suggest that the occupancies are only slightly different for **II** and **IV** (13 and 16%, respectively), the composition being confirmed by the stoichiometric synthesis of the phase-pure sample only in the former case, and differ significantly from the 40% population in $[Hg_6As_4](HgCl_6)Hg_{0.4}$ [2a] and 60% population in $[Hg_6As_4](FeBr_6)Hg_{0.6}$.[6] It could be that the population is sensitive both to the synthetic conditions and to the extent of the host-guest mismatch; this is currently being investigated.

As was described above, the SnX_3^- anions encapsulated in the framework cavities are not covalently bonded to the host structure (Figure 2), the host-guest interactions being limited to very weak electrostatic forces. Having a family of phases with similar crystal structures, we can now estimate

Table 7. Selected interatomic distances and bond angles for **V**

Distances [Å]	
Sn(1)−Br(2)	2.722(4) ×3
P(1)−Hg(1)	2.366(13)
P(1)−Hg(2)	2.414(2) ×3
P(2)−Hg(1)	2.385(15)
P(2)−Hg(3)	2.399(4) ×3
P(3)−P(4)	2.18(2)
P(3)−Hg(3)	2.422(5) ×3
P(4)−Hg(2)	2.428(4) ×3
Hg(2)−Br(1)	2.981(3)
Hg(3)−Br(1)	3.129(3)
Hg(2)−Br(2)	3.142(3)
Hg(2)−Br(2)	3.364(3)
Hg(3)−Br(2)	3.352(3)
Angles [°]	
Br(2)−Sn(1)−Br(2)	91.27(14) ×3
Hg(1)−P(1)−Hg(2)	98.5(3) ×3
Hg(2)−P(1)−Hg(2)	117.84(15) ×3
Hg(1)−P(2)−Hg(3)	107.0(3) ×3
Hg(3)−P(2)−Hg(3)	111.8(3) ×3
P(4)−P(3)−Hg(3)	110.7(3) ×3
Hg(3)−P(3)−Hg(3)	108.2(3) ×3
P(3)−P(4)−Hg(2)	108.4(3) ×3
Hg(2)−P(4)−Hg(2)	110.5(3) ×3
P(1)−Hg(1)−P(2)	180.0(2)
P(1)−Hg(2)−P(4)	166.6(4)
P(2)−Hg(3)−P(3)	176.0(3)

how these weak interactions influence the structural organization and formation of these compounds. As a first step, we shall discuss the problem of size matching between the cavity of the cationic framework and the guest anion, as well as the slight structural changes in the host structure that this mismatch may cause. Then we shall show how the cavity configuration influences the geometry of the guest anion through weak electrostatic forces. It should be noted that the quality of the structural data differs from one compound to another — as can be seen from Table 2 — the structures of the compounds **I** and **V** being less accurate. However, since the discussion of the host-guest interaction is semi-quantitative, the achieved accuracy of the structural data seems to be sufficient.

In the structures of **I** and **II**, the same SnCl$_3^-$ ion occupies the cavities of the [Hg$_6$P$_4$Cl$_3$]$^{1+}$ and [Hg$_6$As$_4$Cl$_3$]$^{1+}$ host frameworks. Evidently, the two frameworks possess cavities of different size (smaller in **I** than in **II**) to trap the same anion. This means that the size of the cavity may vary within a certain range, whilst still remaining appropriate for anions of the same size. Comparing **III** and **V**, one can see that the SnBr$_3^-$ anion fits into the cavity of the [Hg$_6$As$_4$Br$_3$]$^{1+}$ framework of **III**, but is too large if arsenic is replaced by phosphorus in the host structure (**V**). In the latter case the SnBr$_3^-$ anion requires a larger cavity in the host framework. Similarly, the SnI$_3^-$ anion fits into the cavity of the [Hg$_6$Sb$_4$I$_3$]$^{1+}$ framework (**IV**), but becomes too large if antimony is replaced by arsenic in the framework (**VI**) and requires an expansion of the host structure. The expansion of the framework in **V** and **VI** occurs by the addition of an extra Hg^{2+} atom which "breaks" every second Z_2^{4-} dumbbell into two discrete Z^{3-} atoms (Figure 3). This leads to the formation of another type of host framework with larger cavities, [Hg$_7$Z$_4$X$_3$]$^{1+}$, and keeps the framework charge unchanged. Due to the severe size mismatch no SnX$_3^-$-containing compounds have been found in the Hg/P/Sn/I, Hg/Sb/Sn/Cl, and Hg/Sb/Sn/Br systems. As is clear from Table 1, the SnCl$_3^-$ and SnBr$_3^-$ anions are too small for the antimony-containing frameworks, whereas the SnI$_3^-$ anion is too large for the phosphorus-containing frameworks, be they of type 1 or 2 (Table 1). The above discussion leads to the following conclusion: the condition of the size matching of the guest anion and the host framework cavity is not too strict but is still important for the formation of the phases under consideration.

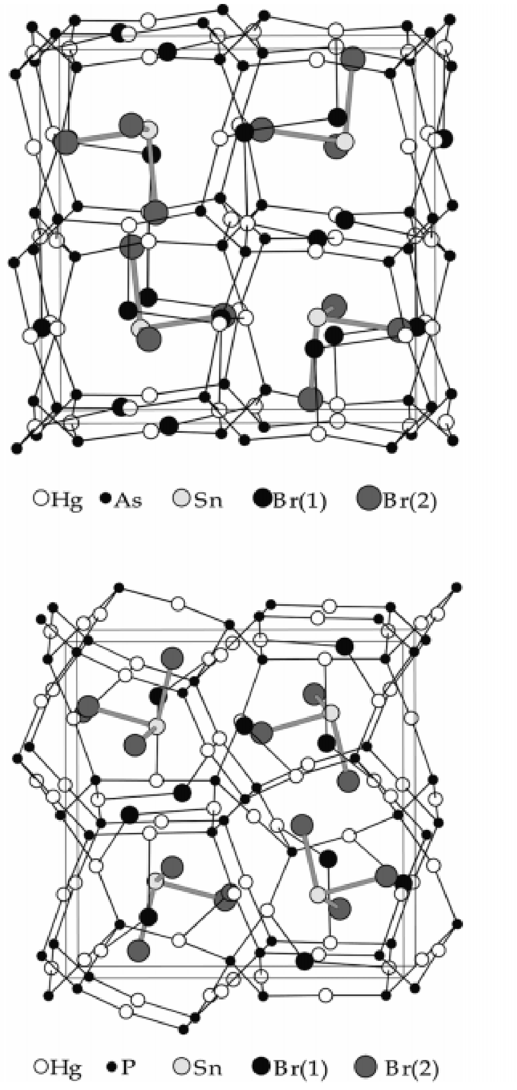

Figure 1. Unit cells of the crystal structures of [Hg$_6$As$_4$Br$_3$](SnBr$_3$) (top) and [Hg$_7$P$_4$Br$_3$](SnBr$_3$) (bottom)

As has already been shown for **VI**,[2e] weak host-guest interactions influence the geometry of the SnI$_3^-$ anion, and the calculated equilibrium geometry of the SnI$_3^-$ anion appeared to differ from that observed in the crystal structure.

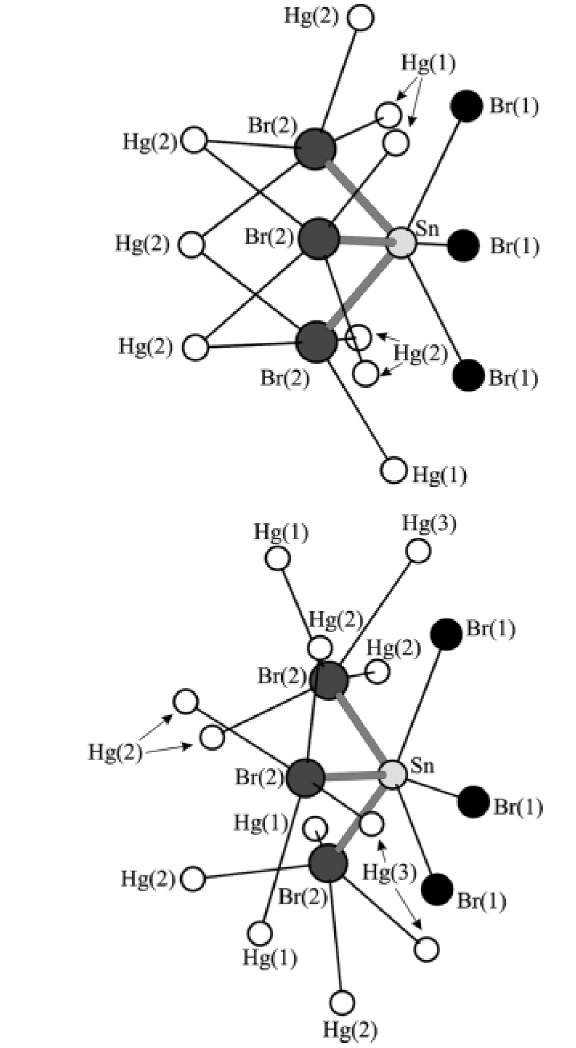

Figure 2. Coordination of the SnX_3^- anion by distant atoms of the host framework in **III** (top) and **V** (bottom)

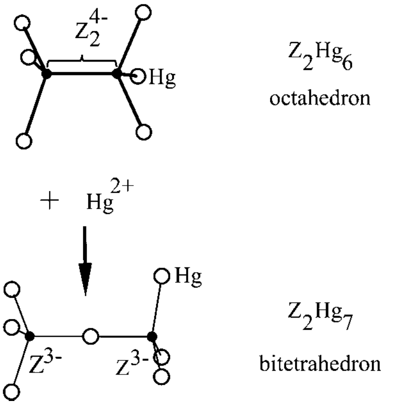

Figure 3. A scheme of the transition from the $[Hg_6Z_4X_3]^+$ framework to the $[Hg_7Z_4X_3]^+$ framework by breaking a Z_2^{4-} dumbbell with a Hg^{2+} cation

In this work we have performed the same level of ab initio calculations for the $SnCl_3^-$ and $SnBr_3^-$ guest anions (see Exp. Sect. for details). The geometry of the SnX_3^- anions found in the crystal structures of **I**−**V** and **VI**,[2e] and the corresponding calculated equilibrium values, are given in Table 8. It is clear that in all crystal structures the Sn−X separations are longer and the X−Sn−X angles are lower than the equilibrium values. A comparison of the observed geometry of the $SnBr_3^-$ guest anion in the structures of **III** and **V**, and of the SnI_3^- anion in **IV** and **VI** with the calculated ones shows that the same guest anion appears to be more distorted in **III** than in **V**, and in **IV** than in **VI**. The reason for such differences is quite apparent. The positive charge of the host cationic framework is "smeared" over the inner surface of the cavities. In **V** and **VI** the cavity has one additional mercury atom which expands its surface. Consequently, the "specific charge" of the cavity is smaller in **V** and **VI** than in the other four phases, and this is why the electrostatic interaction between the host and guest is weaker in **V** and **VI**. In turn, the weaker host-guest interaction causes a less-pronounced departure of the observed geometry from the equilibrium. A comparison of **I** and **II** shows that they possess an identical type of framework, and although the size of these frameworks is different, the observed geometry of the $SnCl_3^-$ anion they trap exhibits the same deviation from equilibrium in both structures. The above discussion leads to the conclusion that the weak electrostatic host-guest interactions primarily control the geometry of the guest SnX_3^- anion and the type of the host framework, provided that the size matching, which is not very strict, is achieved.

The nature of the weak electrostatic host-guest interaction is not discussed in this article. Recently[7] we showed that for similar supramolecular complexes containing d-metals as the centers of guest anions a host-guest charge transfer takes place.

Concluding Remarks

The above-described family of compounds illustrates features important for understanding the principles of the formation of solid state supramolecular complexes. Evidently, new compounds in the Hg/Z/Sn/X systems form only if the host-guest complementarity, which includes the geometry/topology matching and charge balance, is achieved. More important is that the mutual adjustment of the host and guest is possible. The supramolecular complexes discussed in this article show that the guest serves as a template for the construction of a host framework of the appropriate size, and changes its own geometry according to the "requirements" of the host. Weak electrostatic forces that exist between charged host and guest control their mutual adjustment.

Experimental Section

Starting Materials: Hg_2Cl_2, Hg_2Br_2, $HgBr_2$, HgI_2, red phosphorus, gray arsenic, antimony, tin powder, and mercury were used for the synthesis and single crystal growth of the reported compounds. All reagents were of high purity (> 99.99%), except for phosphorus (97%), which was purified as described elsewhere.[2e]

Table 8. Geometry of SnX_3^- as found and calculated

Anion	in compound		d(Sn−X)/Å and (X−Sn−X)/deg.	
			from structure	calculated
$SnCl_3^-$	$[Hg_6P_4Cl_3]SnCl_3$	**(I)**	2.62 Å, 86.9°	2.49 Å, 96.6°
	$[Hg_6As_4Cl_3](SnCl_3)Hg_{0.13}$	**(II)**	2.63 Å, 87.7°	
$SnBr_3^-$	$[Hg_7P_4Br_3]SnBr_3$	**(V)**	2.71 Å, 91.5°	2.66 Å, 97.8°
	$[Hg_6As_4Br_3]SnBr_3$	**(III)**	2.77 Å, 87.5°	
SnI_3^-	$[Hg_7As_4I_3]SnI_3$	**(VI)**	2.95 Å, 90.9°	2.90 Å, 99.2°
	$[Hg_6Sb_4I_3](SnI_3)Hg_{0.16}$	**(IV)**	2.99 Å, 88.1°	

Synthesis: Compounds **I**, **II** and **III** were prepared from stoichiometric mixtures (approx. 1 g.) of the respective mercury(I) halide, pnicogen, and tin powder, which were heated for five days at 400 °C in vacuum-sealed silica tubes. The samples formed as yellow (**I**) or dark-red (**II** and **III**) air-stable polycrystalline powders, but did not contain single crystals suitable for a structure determination. A profile analysis of the diffraction patterns of the samples [STADI-P (STOE), Cu-$K_{\alpha1}$ radiation] confirmed that they were phase-pure. For the X-ray crystal structure analysis, single crystals of **I**, **II**, and **III** were selected from the samples prepared from the mixtures of the respective mercury(I) halide, phosphorus (arsenic), tin powder, and mercury in a 3:4:1:1 molar ratio. The mixtures (total weight approx. 1 g) were vacuum-sealed in silica ampoules and heated at 400 °C for five days.

For the preparation of **IV**, mercury(II) iodide, antimony, tin powder, and mercury were mixed in a 3:4:1:4 ratio. Approximately 1 g of this mixture was heated for five days at 500 °C in an evacuated silica ampoule. The product formed as a mixture of a new black phase and liquid mercury, and contained single crystals suitable for a structure determination.

Compound **V** was prepared by heating a stoichiometric mixture of mercury(II) bromide, red phosphorus, tin powder, and mercury in a vacuum-sealed silica tube for two days at 400 °C. The sample appeared as a crop of yellow crystals of different shapes and sizes. Only a small admixture of unchanged starting materials was detected by X-ray powder diffraction.

No new compounds were obtained from the Hg/P/Sn/I, Hg/Sb/Sn/Cl and Hg/Sb/Sn/Br systems upon annealing samples with the composition $3HgI_2$:4P:1Sn, $3Hg_2Cl_2$:4Sb:1Sn, and $3Hg_2Br_2$:4Sb:1Sn for five days, and varying the temperature from 400 to 500 °C.

Crystal Structure Determinations: Suitable single crystals of **I**−**V** were mounted on a CAD-4 (Nonius) goniometer head. The cubic unit cell parameters were refined based on 24 well-centered reflections in the angular range $12° < \theta < 17°$. All data sets were collected at ambient temperature with the data collection parameters listed in Table 2. A semiempirical absorption correction was introduced based on azimuthal scans of not less than six reflections with χ angles close to 90°. Analysis of the systematic absences in the data sets revealed two possible space groups $P2_13$ (no. 198) and $P4_232$ (no. 208). For the structure solution, following the presumed analogy with the synthesized earlier compound $[Hg_7As_4I_3](SnI_3)$, the space group of lower symmetry was chosen in all cases. The atomic positions of mercury, iodine, antimony, tin, bromine and arsenic atoms in all the structures were estimated by direct methods (SHELXS-97).[8] The phosphorus and chlorine atoms were localized by a sequence of $\Delta\rho$(xyz) syntheses and least-squares cycles (SHELXL-97).[9] During the refinement of the crystal structures of **II** and **IV** an electron density peak was observed residing in the smaller cavity of the host framework. The position of this peak was refined as being partly occupied by mercury. Final anisotropic full-matrix refinement on F^2 led to satisfactory R_1 and wR_2 values as listed in Table 2. Attempts to solve the structures in the space group $P4_232$ did not lead to reasonable solutions.

It should be noted that the quality of the reflections that were used for the absorption correction procedure in the case of **I** was rather low. We consider this to be the reason why one of the phosphorus atoms has abnormally weak thermal displacement parameters. Unfortunately, due to the irregular shape of the crystal, the numerical absorption correction was unsuccessful.

Further details of the crystal structure determination may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD-411863 (**I**), -411862 (**II**), -411861 (**III**), -411859 (**IV**), and -411860 (**V**).

Computational Aspects: Ab initio RHF calculations were performed using the GAMESS-US[10] program. SBKJC effective core potentials were applied to all atoms and the SBKJC basis set[11] implemented in GAMESS was used. The starting geometry of the $SnCl_3^-$ and $SnBr_3^-$ anions was taken from the crystal structure refinement of **I** and **III**, respectively. The geometry of the SnX_3^- anions was optimized without any constraints (C_{3v} and C_s symmetries). Geometry optimizations were performed by the quasi-Newton algorithm[12] implemented in GAMESS. In all cases the optimized geometries did not depend on the point symmetry group applied to the SnX_3^- ion. The hessian computations and normal vibration analyses showed all stationary points located to be minima.

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