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Reduction of the Host Cationic Framework Charge by Isoelectronic Substitution: Synthesis and Structure of $Hg_7Ag_2P_8X_6$ (X = Br, I) and $Hg_6Ag_4P_8Br_6$

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The first compounds, $Hg_7Ag_2P_8X_6$ (X = Br, I) and $Hg_6Ag_4P_8Br_6$, featuring the partial isoelectronic substitution of Hg^{2+} for Ag^{1+} in mercury–pnicogen frameworks have been obtained and structurally characterized. The new compounds are the supramolecular assemblies built of the covalently bonded metal–pnicogen frameworks trapping guests of different complexity. The frameworks feature the perfect ordering of Hg^{2+} and Ag^{1+} cations and contain P_2^{4-} and P_6^{6-} phosphorus clusters. The substitution of Hg^{2+} with Ag^{1+} leads to the reduction in charge of the host cluster-containing cationic matrix and concomitant replacement of the monatomic X^- guest by a lesser amount of the $AgBr_3^{2-}$ anions.

The design and characterization of inorganic supramolecular assemblies with controlled host−guest interactions is a challenging mission promising the creation of new compounds and materials on the basis of the recognition process. Careful design of the host frameworks capable of trapping guest ions or molecules due to the host−guest charge, topology, and geometry match is a key to the construction of such solids.[1] A broad family of supramolecular assemblies based on the mercury−pnicogen (Pn = P, As, Sb) frameworks has been extensively studied[2] in the past decade. Such frameworks are built on the linearly coordinated mercury and tetrahedraly coordinated pnicogen atoms and conform to a general formula $[Hg_nPn_m]^{m+}$. The positively charged 3D host matrixes possess nanosized cavities of different shapes that are occupied by various discrete[3] and infinite[4] anionic guests ranging from halides to halometalate anions. Thus far, a great variety of halometalate anions, containing p,[5] d,[2,6] and f centers[7] have been embedded into the framework cavities of complementary topology. At the same time, an introduction of any heteroatoms into the mercury−pnicogen matrix itself has never been observed. Obviously, the charge of the framework can be reduced by partial substitution of Hg^{2+} by M^{1+} centers. A certain degree of substitution will result in the formation of neutral frameworks with empty cavities capable of trapping neutral guests. Silver seems to be the perfect candidate for such a replacement since it is known[8] to maintain a similar linear coordination in the oxidation state 1+. However, we have demonstrated earlier[3,4] that, when Pn = As, the silver ions do not replace mercury in a framework rather participating in the formation of the guest halometalate counteranions. In this work, we report the first case of partial isoelectronic substitution of Hg^{2+} by Ag^{1+} in the host framework that leads to reduction of its charge.

$Hg_7Ag_2P_8Br_6$ and $Hg_7Ag_2P_8I_6$ were prepared[9] by a standard ampule technique. The products appeared as black air-stable polycrystalline powders. The crystal structure[10] of $Hg_7Ag_2P_8X_6$ (X = Br, I) is shown in Figure 1. In this unique type of crystal structure, mercury, silver, and phosphorus atoms form a 3D framework, while bromine or iodine atoms fill the channels. Within the framework, the phosphorus atoms form two types of polyanions, P_2 dumbbells and P_6 rings in the chair conformation. Each phosphorus atom of a

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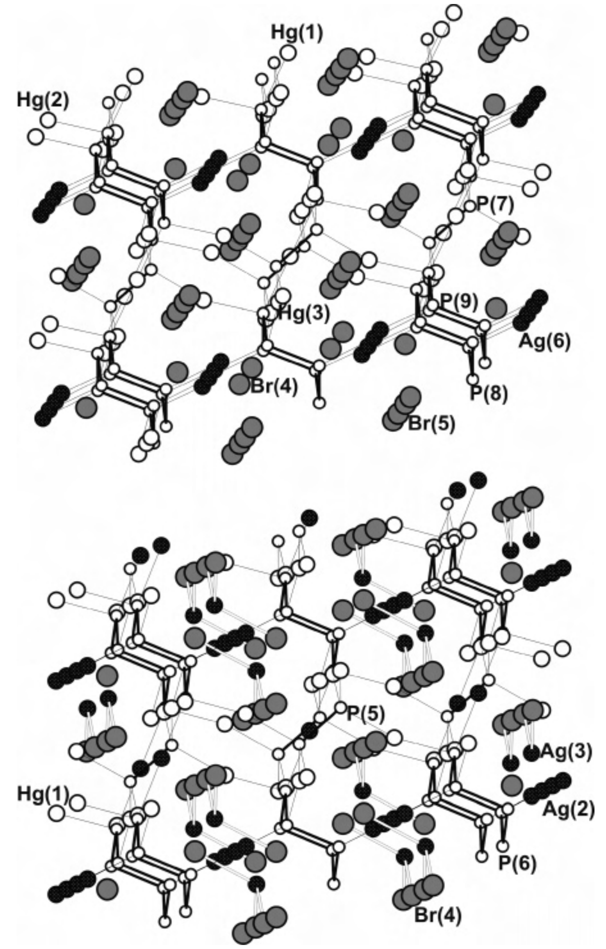

Figure 1. Crystal structure of $Hg_7Ag_2P_8Br_6$ slightly off the *b* axis (top) and $Hg_6Ag_4P_8Br_6$ slightly off the *a* axis (bottom). The atom labeling corresponds to the Table 1.

Table 1. Selected Bond Distances (Å) and Angles (deg) for $Hg_7Ag_2P_8Br_6$, $Hg_7Ag_2P_8I_6$, and $Hg_6Ag_4P_8Br_6$

$Hg_7Ag_2P_8Br_6$

Distances

Hg(1)−P(8)	2.497(3) × 2	Ag(6)−P(9)	2.579(2) × 2
Hg(1)−Br(5)	3.0882(9) × 4	Ag(6)−Br(5)	2.952(1)
Hg(2)−P(7)	2.391(3)	Ag(6)−Br(4)	3.0547(7) × 2
Hg(2)−P(8)	2.415(3)	P(7)−P(7)	2.149(6)
Hg(2)−Br(4)	3.034(1)	P(8)−P(9)	2.202(3) × 2
Hg(3)−P(7)	2.396(1)	P(9)−P(9)	2.209(5)
Hg(3)−P(9)	2.412(2)		

Angles

P(8)−Hg(1)−P(8)	180.0	P(9)−Ag(6)−P(9)	180.0
P(7)−Hg(2)−P(8)	162.0(1)	P(9)−P(8)−P(9)	102.2(1)
P(7)−Hg(3)−P(9)	164.64(9)	P(8)−P(9)−P(9)	105.4(1)

$Hg_7Ag_2P_8I_6$

Distances

Hg(1)−P(8)	2.600(4) × 2	Ag(6)−P(9)	2.679(3) × 2
Hg(1)−I(5)	3.1076(8) × 4	Ag(6)−I(5)	2.9869(9) × 2
Hg(2)−P(7)	2.434(5)	Ag(6)−I(4)	3.0686(6)
Hg(2)−P(8)	2.448(4)	P(7)−P(7)	2.167(9)
Hg(2)−I(4)	3.194(1)	P(8)−P(9)	2.216(4) × 2
Hg(3)−P(7)	2.433(3)	P(9)−P(9)	2.216(6)
Hg(3)−P(9)	2.436(3)		

Angles

P(8)−Hg(1)−P(8)	180.0	P(9)−Ag(6)−P(9)	180.0
P(7)−Hg(2)−P(8)	162.8(1)	P(9)−P(8)−P(9)	104.0(2)
P(7)−Hg(3)−P(9)	163.5(1)	P(8)−P(9)−P(9)	106.6(1)

$Hg_6Ag_4P_8Br_6$

Distances

Hg(1)−P(5)	2.404(4)	Ag(2)−Br(4)	2.844(5) × 2
Hg(1)−P(6)	2.425(8)	Ag(3)−Br(4)	2.728(5) × 3
Ag(2)−P(6)	2.54(1)	P(5)−P(5)	2.17(2)
Ag(2)−P(6)	2.59(1)	P(6)−P(6)	2.198(9) × 2

Angles

P(5)−Hg(1)−P(6)	165.3(3)	Br(4)−Ag(3)−Br(4)	108.4(2) × 3
P(6)−Ag(2)−P(6)	166.4(3)	P(6)−P(6)−P(6)	102.2(4)

dumbbell has one homonuclear single bond[11] ranging from 2.15 to 2.21 Å (Table 1) and is further connected to three mercury atoms, whereas each phosphorus atom of a six-member ring forms two homonuclear bonds and is bound to two metal atoms. Thus, all phosphorus atoms possess more or less distorted tetrahedral coordination, and according to the number of the P−P and P−M bonds, the phosphorus polyanions can be formulated as P_2^{4-} and P_6^{6-}. The mercury and silver atoms connecting phosphorus anionic clusters are perfectly ordered within the framework. The metal centers occupy different sites and show significant difference in the M−P bonding distances. The Hg−P separations are 0.1−0.25 Å shorter than the Ag−P ones, the minimal *d*(Hg−P) value being 2.39 Å, which is normal, taking into account the propensity of mercury to admix d orbitals into the Hg−P bonding,[12] whereas the Ag−P bond distances of 2.58−2.68 Å are the same as those found in silver polyphosphides.[13,14] At the same time, the mercury and silver atoms have similar coordination. Each metal bridges two phosphorus atoms with the P−Ag−P angles being exactly 180° and the P−Hg−P angles ranging from 162° to 180°. Noteworthy, the ideal linear coordination pertains to the Ag and Hg atoms bridging phosphorus atoms of neighboring P_6^{6-} chair cycles. Coordination of mercury and silver points to their typical oxidation states, Hg(II) and Ag(I); consequently, the framework is formulated as $[Hg^{II}_7Ag^{I}_2P_2^{4-}P_6^{6-}]^{6+}$, which requires exactly six halogen anions to achieve electroneutrality for the whole assembly.

$Hg_6Ag_4P_8Br_6$ was found as a byproduct in the synthesis of $Hg_7Ag_2P_8Br_6$ at higher temperature, and its composition was confirmed by the EDX analysis.[15] It is not isomorphous to the latter; however, the geometry of the host frameworks in two structures appears to be very similar (Figure 1). The difference is the replacement of the Hg atom at the origin

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(10) Crystal data for $Hg_7Ag_2P_8Br_6$: $M_r = 2347.08$, *C*2/*m* (no. 12), $a = 12.8660(17)$ Å, $b = 10.9562(17)$ Å, $c = 8.0792(12)$ Å, $\beta = 100.902(3)°$, $V = 1118.3(3)$ Å^3, $Z = 2$, $T = 173(2)$ K, μ(Mo Kα) = 60.842 mm^{-1}, 4749/1382 reflns measured/unique ($R_{int} = 0.0644$). The final R1 = 0.0374, wR2 = 0.0968 for all data. For $Hg_7Ag_2P_8I_6$: $M_r = 2629.04$, *C*2/*m* (no. 12), $a = 13.1464(17)$ Å, $b = 11.0370(14)$ Å, $c = 8.3358(11)$ Å, $\beta = 102.210(2)°$, $V = 1182.1(3)$ Å^3, $Z = 2$, $T = 173(2)$ K, μ(Mo Kα) = 55.252 mm^{-1}, 5071/1447 reflns measured/unique ($R_{int} = 0.0299$). The final R1 = 0.0388, wR2 = 0.0924 for all data. For $Hg_6Ag_4P_8Br_6$: $M_r = 2362.24$, $R\bar{3}m$ (no. 166), $a = 10.8320(4)$ Å, $c = 16.5125(12)$ Å, $V = 1677.88(15)$ Å^3, $Z = 3$, $T = 173(2)$ K, μ(Mo Kα) = 55.70 mm^{-1}, 4858/521 reflns measured/unique ($R_{int} = 0.0292$). The final R1 = 0.0463, wR2 = 0.1657 for all data.

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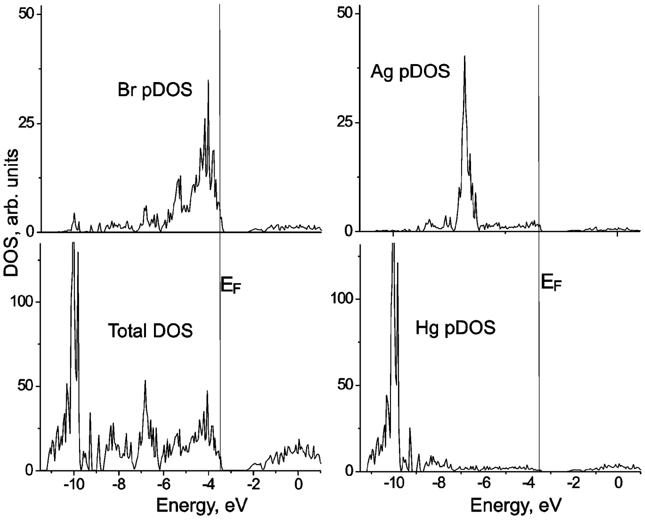

Figure 2. Density of states (DOS) plots for $Hg_7Ag_2P_8Br_6$. Vertical lines mark the Fermi level.

(Hg(1) in $Hg_7Ag_2P_8Br_6$) by the silver atom. This obviously leads to further reduction in the charge of the host framework that is formulated as $[\mathrm{Hg^{II}}_6\mathrm{Ag^{I}}_3\mathrm{P_2}^{4-}\mathrm{P_6}^{6-}]^{5+}$. Clearly, one of the silver atoms per $Hg_6Ag_4P_8Br_6$ formula does not belong to the host matrix and constitutes a part of the guest substructure.

In the structure of $Hg_7Ag_2P_8X_6$, the halogen atoms reside in the channels of the framework, completing the coordination of the metal atoms by distant contacts, the shortest atomic separation being 2.9 Å for X = Br and 3.1 Å for X = I. In such a way, the monocapped octahedral coordination of mercury or distorted octahedral coordination of silver and mercury are achieved. The halogen atoms possess seven distant neighbors at the maximal distance of 3.7 Å for X = Br and 3.8 Å for X = I. With such coordination, the halogens can be regarded as the X^- anions, and the whole compound can be written as $[Hg_7Ag_2P_8]X_6$, emphasizing its pseudo-ionic construction. In the structure of $Hg_6Ag_4P_8Br_6$, the guest substructure consists of silver and bromine atoms. The bromine atoms occupy the same positions inside the channels of the host framework as in the crystal structure of $[Hg_7Ag_2P_8]X_6$. The silver atom Ag(4) introduces into the guest substructure such that it has three relatively close bromine neighbors, $d(\mathrm{Ag{-}Br}) = 2.73$ Å. It is further connected to three more distant phosphorus and silver atoms of the framework, thus forming a very irregular 9-vertex polyhedron. The position of the Ag(4) atom is only 50% occupied; consequently, the compound can be formulated as $[Hg_6Ag_3P_8]AgBr_6$.

The results of the band structure calculations[16] contradict somehow with the simplified ionic model of the title compounds because the occupied anion bands are located higher on the energy scale than the majority of the 3D cation filled states. The states in vicinity of the Fermi level (Figure 2) contain mainly p orbitals of halogen atoms and are the lone pairs of the bromide anion. On going from bromine to iodine, the calculated band gap decreases from 1.0 to 0.8 eV, which is consistent with the rise in the orbital energy of p states. Analysis of the orbital contributions (projected density of states (DOS), Figure 2) reveals that the Hg−Br and Ag−Br host−guest interactions are relatively weak and diffuse while the Ag−P and especially Hg−P interactions are strong. However, it can be assumed that the large number of weak M−Br (M = Hg or Ag) interactions ensures the proper positioning of the bromine atoms inside the channels of the cationic framework, precluding positional disorder and making the ionic mobility very improbable. The mobility, in particular the possibility to exchange or remove the guest anions, was not tested in this work; it should be noted, however, that the charged framework cannot exist without the charge-compensating guests. Therefore, the title compounds can be formed only through a self-assembling in the course of the synthesis from preformed moieties.[2]

The title compounds show the conservation of the structural motif upon replacement of mercury by silver in the framework. The only structural difference is the implantation of an extra silver atom into the guest substructure, which is necessary to achieve the electroneutrality of the assembly. The compounds might be seen as the members of the series built on the $[Hg_{9-x}Ag_xP_8]^{(8-x)+}$ framework. However, the end members of this family cannot be obtained since the Hg-free framework would possess a negative charge, whereas the Ag-free framework would require eight halides to compensate for the positive charge but the space in the structure is available only for six atoms.

In conclusion, $Hg_7Ag_2P_8Br_6$, $Hg_7Ag_2P_8I_6$, and $Hg_6Ag_4P_8Br_6$ are the first compounds featuring the incorporation of silver into the Hg−P cationic framework. Their structures exhibit an ordered distribution of the Ag^+ and Hg^{2+} cations. The substitution of Ag^+ for Hg^{2+} having similar coordination but different formal charge leads to diminution in the charge of the host matrix. Furthermore, the combination of these cations favors the formation of rather complex phosphorus substructures featuring P_6^{6-} chairs in addition to known P_2^{4-} dumbbells. In general, the heterovalent substitution supported by the knowledge of the structure of main building blocks can be a powerful tool for the design and synthesis of the supramolecular solid-state assemblies with the controlled charge of the framework.

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Supporting Information Available: A CIF file containing information on three structural experiments and the complete description of the syntheses. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Band structure calculations were performed for $Hg_7Ag_2P_8Br_6$ and $Hg_7Ag_2P_8I_6$ using the TB-LMTO-ASA approach. Before the calculation of DOS, the SCF calculations were performed for 96 k-points in the irreducible Brillouin zone.