Synthesis and Crystal Structures of $Hg_6Sb_5Br_7$, $Hg_6As_4BiCl_7$, and $Hg_6Sb_4BiBr_7$, Built of a Polycationic Mercury-Pnictide Framework with Trapped Anions

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$Hg_6Sb_5Br_7$, $Hg_6As_4BiCl_7$, and $Hg_6Sb_4BiBr_7$ were prepared from stoichiometric mixtures of Hg_2X_2, HgX_2 ($X = Cl$, Br), As, Sb, and Bi in sealed, evacuated glass ampoules in temperature gradients $260 \rightarrow 240°C$ for $Hg_6Sb_5Br_7$, $340 \rightarrow 320°C$ for $Hg_6As_4BiCl_7$, and $290 \rightarrow 270°C$ for $Hg_6Sb_4BiBr_7$. All compounds crystallize in the cubic space group $Pa\bar{3}$ with $Z = 4$ and the lattice constants $a = 13.003(1)$ Å for $Hg_6Sb_5Br_7$, $a = 12.178(2)$ Å for $Hg_6As_4BiCl_7$, and $a = 12.998(4)$ Å for $Hg_6Sb_4BiBr_7$. The structures have been solved based on single-crystal X-ray diffraction data and refined to $R(F) = 0.0431$, 666 F_o for $Hg_6Sb_5Br_7$, $R(F) = 0.0478$, 690 F_o for $Hg_6As_4BiCl_7$, and $R(F) = 0.0444$, 840 F_o for $Hg_6Sb_4BiBr_7$ with 30 parameters for each refinement. The structures are characterized by a three-dimensional polycationic framework of pnictide dumb-bells (As–As distance 2.43 Å, Sb–Sb distance 2.78 Å), each connected by six mercury atoms to six neighbored As_2/Sb_2 groups. There are two different cages in the framework; one type is occupied by nearly regular MX_6 octahedra ($M = Sb, Bi; X = Cl, Br$), the other by halide ions. The three compounds crystallize closely related to $Cd_7P_4Cl_6$, which contains a similar polycationic framework of P_2 dumb-bells connected by Cd, but with only one type of cage occupied by octahedral $[CdCl_6]^{4-}$ ions. The interactions between the atoms of the polycationic framework and the anions are very weak. The observed diamagnetism of all three compounds is in agreement with the ionic formulas $(Hg_6Sb_4)^{4+}[SbBr_6]^{3-}Br^-$, $(Hg_6As_4)^{4+}[BiCl_6]^{3-}Cl^-$, and $(Hg_6Sb_4)^{4+}[BiBr_6]^{3-}Br^-$. © 2000 Academic Press

INTRODUCTION

The pnictide halides of mercury and cadmium are a class of solid state compounds with a remarkable diversity of structural features. The oxidation state of the pnictogen atoms plays a key role for their connectivity and the structure type. In the structural family M_2Y_3X ($M = Cd$, Hg;

$Y = P$, As, $X = Cl$, Br, I) (1–4) the oxidation state -1 is present. In these compounds the pnictogen atoms have six valence electrons and act as pseudoelements of group 16, forming infinite chains. The oxidation state of the pnictogen atom can be supposed being -2 in M_2YX_2 (5), $M_7Y_4X_6$ (6), and $Hg_5Sb_2I_6$ (7) ($M = Cd$, Hg; $Y = P$, As, Sb; $X = Cl$, Br, I). Here, the pnictogen atoms form P_2, As_2, or Sb_2 dumb-bells that are connected by Cd or Hg atoms. The oxidation state -3 is equivalent to eight valence electrons on the pnictide ion. As a consequence no homonuclear bonds are observed in compounds like M_3YX_3 (8) ($M = Cd$, Hg; $Y = P$, As, Sb; $X = Cl$, Br, I). The pnictogen atoms are tetrahedrally coordinated by four Cd or Hg atoms. Compounds with composition $M_4Y_2X_3$ (9, 10) are of mixed valency and contain both Y_2 dumb-bells and M_4Y tetrahedra as structural units. Less is known about quaternary phases. $Hg_9As_4Bi_2Br_{12}$ (11) is the only representative found in the literature.

We succeeded in synthesizing the new ternary mercury pnictide halide $Hg_6Sb_5Br_7$ and the quaternary compounds $Hg_6As_4BiCl_7$ and $Hg_6Sb_4BiBr_7$ whose structures are closely related to that of $Cd_7P_4Cl_6$. The recently reported chloride $Hg_{7.4}As_4Cl_6$ (12) also belongs to this structural family. We show that $Hg_7Sb_4Br_6$ (13), which was recently published with a disordered structure, can be described differently without disorder and is obviously identical to $Hg_6Sb_5Br_7$.

EXPERIMENTAL

Syntheses

The following starting materials were used: $HgCl_2$ (Fluka 99.5%), Hg_2Cl_2 (Fluka 99.5%), $HgBr_2$ (Fluka 98%), Bi (Aldrich 99.95%), As (Alfa 95.5%), and Sb (Riedel-de-Haën 99.995%). Arsenic and antimony were sublimated twice prior to use and kept, like bismuth, under argon.

$Hg_6Sb_5Br_7$ was prepared by heating a mixture of mercury dibromide, elemental mercury, and antimony (molar

ratio 7/5/10) in a sealed, evacuated glass ampoule. After seven days in a temperature gradient from 260 to 240°C black crystals of cubic shape were deposited in the colder part of the ampoule.

$Hg_6As_4BiCl_7$ is obtained in the form of dark red, cube-like crystals in the colder part of a sealed ampoule when heating a mixture of mercury(I)chloride, mercury(II)chloride, elemental arsenic, and bismuth (molar ratio 5/2/8/2) for three days in a temperature gradient from 340 to 320°C.

The reaction of mercury(II)bromide, elemental mercury, antimony, and bismuth (molar ratio 7/5/8/2) in a sealed evacuated ampoule exposed to a temperature gradient of 290 to 270°C yield after seven days black crystals of $Hg_6Sb_4BiBr_7$ in the colder part of the glass tube.

All three compounds are formed in almost quantitative yield. After two weeks the contents of the reaction ampoules were completely transported to the colder part, leaving only small residues of nonvolatile materials, probably oxidic impurities in the starting materials. Guinier powder diffraction diagrams showed only reflections of the cubic phases. All compounds have a limited thermal stability. Above 450°C a total decomposition into metallic Hg, AsX_3/SbX_3, and mercury halides is observed.

Magnetic Properties

The magnetic properties of all compounds were investigated with the aid of a Faraday balance in the temperature range -196 to $27°C$ (77–300 K). The samples of 0.15 g in weight were filled in silica tubes of 1.5 mm in diameter; the balance was calibrated with $CoHg(SCN)_4$.

Structure Determinations

To avoid hydrolysis by atmospheric moisture single crystals of all compounds were selected in an argon-filled glove box and sealed in glass capillaries of diameter 0.3 mm. Crystals of the following dimensions were chosen: $0.038 \times 0.076 \times 0.056$ mm^3 for $Hg_6Sb_5Br_7$, $0.076 \times 0.114 \times 0.076$ mm^3 for $Hg_6As_4BiCl_7$, and $0.038 \times 0.038 \times 0.114$ mm^3 for $Hg_6Sb_4BiBr_7$. Precession photographs revealed the cubic symmetry. Intensity data collections were performed with a STOE image plate diffractometer using graphite monochromatized MoKα radiation. Systematic absences led to space group $Pa\bar{3}$ for all three crystals. The structures were solved by direct methods (14), showing the positions of all mercury and pnictogen atoms. The positions of halogen atoms were taken from difference Fourier maps. The structural models were refined with full matrix least-square techniques based on F_o^2 with anisotropic displacement parameters for all atoms (15). Due to the high absorption coefficients (605 cm^{-1} for $Hg_6Sb_5Br_7$, 688 cm^{-1} for $Hg_6As_4BiCl_7$, 673 cm^{-1} for $Hg_6Sb_4BiBr_7$) numerical absorption corrections were applied to all data sets. The crystal shapes were optimized with the aid of the program HABITUS (16).

Crystallographic data and details of the data collections are summarized in Table 1. Positional and isotropic

TABLE 1
Crystallographic Data, Data Collection, and Structure Refinement for $Hg_6Sb_5Br_7$, $Hg_6As_4BiCl_7$, and $Hg_6Sb_4BiBr_7$

	$Hg_6Sb_5Br_7$	$Hg_6As_4BiCl_7$	$Hg_6Sb_4BiBr_7$
Crystal system	cubic	cubic	cubic
Space group	$Pa\bar{3}$	$Pa\bar{3}$	$Pa\bar{3}$
Lattice constants	$a = 13.003(1)$ Å	$a = 12.178(2)$ Å	$a = 12.998(4)$ Å
Volume	2198.6 Å^3	1806.0 Å^3	2196.0 Å^3
Z	4	4	4
Density (calc.)	7.165 g/cm^3	7.210 g/cm^3	7.437 g/cm^3
2θ range	$11° < 2\theta < 55.9°$	$11° < 2\theta < 56.2°$	$11° < 2\theta < 56.2°$
Number of reflections collected	16216	16150	16479
Number of unique reflections;	882	731	890
$R_{merge}(F_o^2)$	0.138	0.0575	0.0661
Number of refined parameters	30	30	30
Final R indices	$R = 0.0673$ for 882 independent reflections and $R = 0.0431$ for 666 reflections with $F_o^2 > 4\sigma(F_o^2)$, $wR(F_o^2) = 0.0840$	$R = 0.0498$ for 731 independent reflections and $R = 0.0478$ for 690 reflections with $F_o^2 > 4\sigma(F_o^2)$, $wR(F_o^2) = 0.1308$	$R = 0.0462$ for 890 independent reflections and $R = 0.0444$ for 840 reflections with $F_o^2 > 4\sigma(F_o^2)$, $wR(F_o^2) = 0.1109$
Largest peak	2.72 e/Å^3	2.29 e/Å^3	$+2.09$ e/Å^3
Largest hole	-1.61 e/Å^3	-2.04 e/Å^3	-1.96 e/Å^3
Goodness-of-fit	1.079	1.065	1.099

TABLE 2
Atomic Coordinates and Equivalent Isotropic Displacements Parameters ($Å^2$) for $Hg_6Sb_5Br_7$, $Hg_6As_4BiCl_7$, and $Hg_6Sb_4BiBr_7$

Atom	Position	x	y	z	B_{eq}
		$Hg_6Sb_5Br_7$			
Hg	24d	0.18617(5)	0.30324(5)	0.45335(5)	3.24(2)
Sb1	8c	0.14723(7)	0.14723(7)	0.14723(7)	1.52(3)
Sb2	8c	0.27082(6)	0.27082(6)	0.27082(6)	1.56(3)
Sb3	4b	$\frac{1}{2}$	0	0	1.66(4)
Br1	24d	0.4491(2)	0.2055(2)	0.0448(2)	2.62(3)
Br2	4a	0	0	0	7.0(2)
		$Hg_6As_4BiCl_7$			
Hg	24d	0.18707(5)	0.30488(5)	0.45466(5)	2.25(3)
As1	8c	0.1541(2)	0.1541(2)	0.1541(2)	1.35(5)
As2	8c	0.2693(2)	0.2693(2)	0.2693(2)	1.38(5)
Bi	4b	$\frac{1}{2}$	0	0	1.86(4)
Cl1	24d	0.4491(4)	0.2114(4)	0.0454(4)	2.30(7)
Cl2	4a	0	0	0	4.7(4)
		$Hg_6Sb_4BiBr_7$			
Hg	24d	0.18602(6)	0.30412(6)	0.45242(5)	3.37(3)
Sb1	8c	0.14621(7)	0.14621(7)	0.14621(7)	1.93(3)
Sb2	8c	0.26983(7)	0.26983(7)	0.26983(7)	1.95(3)
Bi	4b	$\frac{1}{2}$	0	0	2.19(3)
Br1	24d	0.4478(2)	0.2086(2)	0.0466(2)	2.74(3)
Br2	4a	0	0	0	5.3(2)

displacement parameters are presented in Table 2; Table 3 contains selected bond lengths and angles.

Further details of the crystal structure analyses are deposited at the *Fachinformationszentrum Karlsruhe*, D-77449 Eggenstein-Leopoldshafen, Germany, and can be obtained by quoting the depository numbers CSD-411219 for $Hg_6Sb_5Br_7$, CSD-411204 for $Hg_6As_4BiCl_7$, and CSD-411218 for $Hg_6Sb_4BiBr_7$.

Chemical Analyses

The compositions of the three compounds have been checked by different methods of chemical analysis.

The presence of Bi in $Hg_6As_4BiCl_7$ and $Hg_6Sb_4BiBr_7$ was confirmed by a qualitative analysis. After dissolution in HNO_3/HCl gaseous H_2S precipitated Hg, As/Sb, and Bi in form of the respective sulfides. On treatment of the mixed precipitates with a solution of $(NH_4)_2S_x$, As_2S_3/Sb_2S_3 dissolved. The residues, consisting of Bi_2S_3 and HgS, were treated with concentrated aqueous HCl which caused the dissolution of Bi_2S_3. In the filtrate Bi was easily detected by reduction to the element with an alkaline $[Sn(OH)_4]^{2-}$ solution.

Crystals of $Hg_6As_4BiCl_7$ were analyzed by X-ray fluorescence (Digital Scanning Microscope DSM 940, Zeiss Corporation, X-ray fluorescence detector by EDAX Int.) and

after dissolution in HNO_3/HCl in a Teflon-lined microwave digestion bomb by inductive-coupled plasma-optical emission spectroscopy (Spectrometer IRIS Advantage, Thermo Jarrell Ash Corporation, Ar plasma). Calculated composition was 0.614 Hg, 0.153 As, 0.107 Bi, 0.127 Cl; found by EDX analysis it was 0.613 Hg, 0.147 As, 0.109 Bi, 0.132 Cl; and found by ICP-OES it was 0.623(1) Hg, 0.152(1) As, 0.104(1) Bi. $Hg_6Sb_5Br_7$ was difficult to analyze since all well-developed crystals contained a small core of a colorless material which is obviously amorphous since no additional reflections in powder diffraction diagrams or in single-crystal diffraction experiments were visible. So crystals were broken before analysis and as much as possible of the small amount of the colorless material was removed mechanically. The gray material was dissolved in HNO_3/HCl and analyzed by ICP-OES. Calculated composition was 0.507 Hg, 0.257 Sb, 0.236 Br; found results were 0.526(1) Hg, 0.245(1) Sb. Since the results of all performed analyses showed the tendency to give on an absolute scale 2.5% too high contents for Hg and 1.5% too low contents for Sb the amorphous accompanying material is probably mercury bromide, which could not be totally removed by mechanical separation.

TABLE 3
Selected Bond Lengths (Å) and Angles (°) for $Hg_6Sb_5Br_7$, $Hg_6As_4BiCl_7$, and $Hg_6Sb_4BiCl_7$

		$Hg_6Sb_5Br_7$	
Hg–Sb1	2.651(1) ($\times 3$)	Sb1–Sb2–Hg	107.19(3) ($\times 3$)
Hg–Sb2	2.650(1) ($\times 3$)	Sb2–Sb1–Hg	111.66(3) ($\times 3$)
Sb1–Sb2	2.784(2)	Hg–Sb1–Hg	111.49(3) ($\times 3$)
Sb3–Br1	2.817(2) ($\times 6$)	Hg–Sb2–Hg	107.37(4) ($\times 3$)
Sb1–Br2	3.316(2) ($\times 2$)	Sb1–Hg–Sb2	165.88(4)
Hg–Br2	3.571(1) ($\times 6$)	Br1–Sb3–Br1	88.40(4) ($\times 3$)
Br1–Br2	3.931(1) ($\times 6$)	Br1–Sb3–Br1	91.60(4) ($\times 3$)
Br1–Hg	3.334(2)		
		$Hg_6As_4BiCl_7$	
Hg-As1	2.512(1) ($\times 3$)	As1–As2–Hg	112.91(5) ($\times 3$)
Hg–As2	2.508(1) ($\times 3$)	As2–As1–Hg	110.55(5) ($\times 3$)
As1–As2	2.429(3)	Hg–As1–Hg	108.38(6) ($\times 3$)
Bi–Cl1	2.705(4) ($\times 6$)	Hg–As2–Hg	105.82(6) ($\times 3$)
As1–Cl2	3.250(3) ($\times 2$)	As1–Hg–As2	165.50(4)
Hg–Cl2	3.338(1) ($\times 6$)	Cl1–Bi–Cl1	88.7(2) ($\times 3$)
Cl1–Cl2	3.611(3) ($\times 6$)	Cl1–Bi–Cl1	91.3(2) ($\times 3$)
Cl1–Hg	3.113(3)		
		$Hg_6Sb_4BiBr_7$	
Hg–Sb1	2.651(1) ($\times 3$)	Sb1–Sb2–Hg	107.17(4) ($\times 3$)
Hg–Sb2	2.649(1) ($\times 3$)	Sb2–Sb1–Hg	112.15(4) ($\times 3$)
Sb1–Sb2	2.783(2)	Hg–Sb1–Hg	111.67(3) ($\times 3$)
Bi–Br1	2.861(2) ($\times 6$)	Hg–Sb2–Hg	106.67(4) ($\times 3$)
Sb1–Br2	3.292(2) (2)	Sb1–Hg–Sb2	165.50(5)
Hg–Br2	3.565(2) ($\times 6$)	Br1–Bi–Br1	88.48(5) ($\times 3$)
Br1–Br2	3.894(2) ($\times 6$)	Br1–Bi–Br1	91.52(5) ($\times 3$)
Br1–Hg	3.336(2)		

RESULTS AND DISCUSSION

The structures of $Hg_6Sb_5Br_7$, $Hg_6As_4BiCl_7$, and $Hg_6Sb_4BiBr_7$ are built of three substructures, first a three-dimensional network of mercury and pnictogen atoms, second slightly distorted octahedral hexahalogeno pnictide anions, and, third discrete halide ions (Fig. 1).

The three-dimensional network consists of pnictide dumb-bells As_2 or Sb_2, which are formed by two crystallographically independent pnictogen atoms. The homonuclear Sb–Sb bond has a short length of 2.783 Å, which is close to that found in $M_4Sb_2I_3$ (M = Hg, Cd) (10) and $Hg_5Sb_2I_6$ (7). The As–As distance of 2.429 Å is typical for compounds containing As_2 groups like $Hg_4As_2I_3$ (9), Cd_2AsCl_2 (17), $Cd_4As_2I_3$ (18), and $Hg_{7.4}As_4Cl_6$ (12). The dumb-bells are each connected by six mercury atoms to six neighboring As_2/Sb_2 groups. The Hg atoms enclose the As_2/Sb_2 groups in the form of a distorted octahedron (Fig. 2). Since these $(As_2/Sb_2)Hg_6$ octahedra are connected by common corners in all directions, the mercury–pnictide substructure adopts the connectivity of the ReO_3 structure type. The approximately linear coordination of Hg with angles As/Sb–Hg–As/Sb of 165° is typical for the oxidation state $+2$. Since the oxidation state of the pnictide ions might be stated being -2 the polycationic framework can be described by the formulas $^3_\infty[Hg_6As_4]^{4+}$ and $^3_\infty[Hg_6Sb_4]^{4+}$.

The three-dimensional network is made up of two crystallographically different cavities of different size. The internal diameter can be defined by the shortest distances between opposite Hg atoms. The larger one with a diameter of about 8.8 Å is filled with a hexahalogeno pnictide ion. The smaller one with a diameter of about 6.7 Å contains a halide ion. The two anions together are arranged in the motif of a rock-
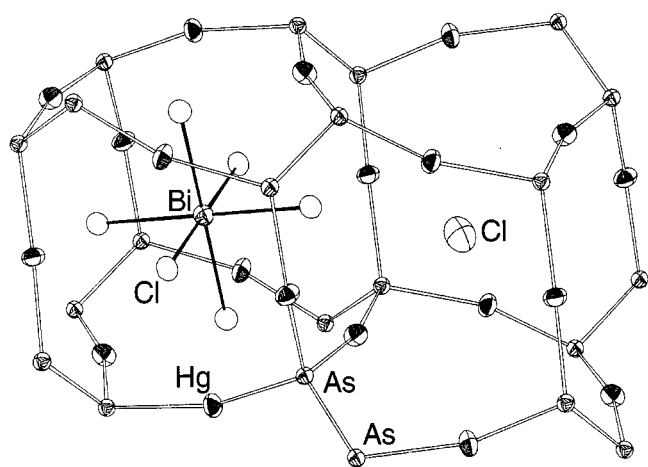

FIG. 2. Cutout of the structure of $(Hg_6As_4)[BiCl_6]Cl$ showing the As_2 dumb-bell and the six nearest Hg atoms forming a distorted octahedron. The thermal ellipsoids are scaled to enclose a probability density of 70%.

FIG. 1. Cutout of the structure of $(Hg_6As_4)[BiCl_6]Cl$. Both types of cavities within the polymeric $^3_\infty[Hg_6As_4]^{4+}$ framework are shown. The smaller cavity is filled with a halide ion, the larger one with the hexachloro bismutate ion. The thermal ellipsoids are scaled to enclose a probability density of 70%.
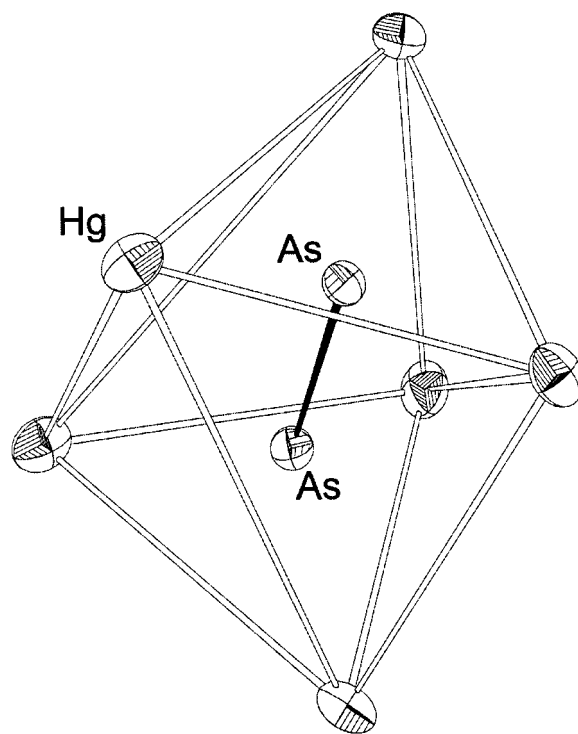
salt structure. The hexahalogeno pnictide ions show only slight distortions from ideal octahedral shape. Due to the crystallographic $\bar{3}$ symmetry the $M–X$ bonds are of equal length. The MX_6 octahedra are slightly compressed along the threefold axis which causes two different $X–M–X$ angles of 88.5° and 91.5° (averaged values). The pnictide–halide bond lengths are in line with the bond lengths for octahedral hexahalogeno–pnictide ions in the respective alkali compounds (Cs_3BiCl_6 (20), Rb_3BiBr_6 (21), $Rb_2Sb_{0.5}$(V) $Sb_{0.5}$(III)Br_6 (22)). Thus, the structures are built of discrete entities, which allow the descriptions as $(Hg_6Sb_4)^{4+}$ $[SbBr_6]^{3-}Br^-$, $(Hg_6As_4)^{4+}[BiCl_6]^{3-}Cl^-$, and $(Hg_6Sb_4)^{4+}$ $[BiBr_6]^{3-}Br^-$. Figure 3 shows the arrangement of the ions in the unit cell.

The determination of the magnetic properties revealed diamagnetism for all three compounds, which is in agreement with these formulas. The observed susceptibilities were nearly temperature independent with $\chi = -476$ to -496×10^{-6} cm^{3}mol^{-1} for $Hg_6Sb_5Br_7$, $\chi = -400$ to -504×10^{-6} cm^{3}mol^{-1} for $Hg_6As_4BiCl_7$, and $\chi = -382$ to -491×10^{-6} cm^{3}mol^{-1} for $Hg_6Sb_4BiBr_7$. These values are in good agreement with calculated susceptibilities (-690×10^{-6} cm^{3}mol^{-1} for $Hg_6Sb_5Br_7$, -638×10^{-6} cm^{3}mol^{-1} for $Hg_6As_4BiCl_7$, -701×10^{-6} cm^{3}mol^{-1} for $Hg_6Sb_4BiBr_7$) obtained by the increment method.
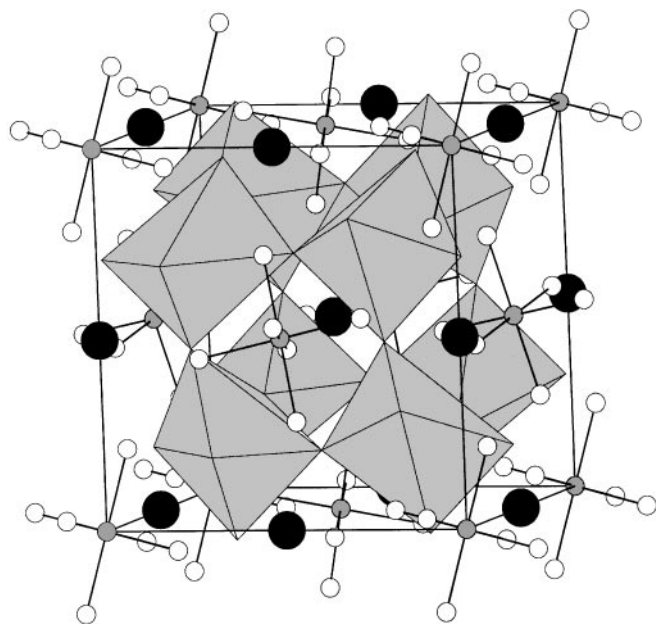
FIG. 3. The unit cell of $(Hg_6Y_4)[MX_6]X$. The ReO_3-type substructure of the polycationic $(Hg_6Y_4)^{4+}$ framework is represented in the form of distorted corner-sharing octahedra. The two different anions occupy the cuboctahedral cavities and are arranged in the motif of a rocksalt structure.

Diamagnetic increments for As($-$II) and Sb($-$II) were obtained by linear extrapolation of the tabulated values for these ions in the oxidation states ($+$III), ($-$III), and ($-$V) (23).

$Hg_6Sb_5Br_7$ and $Hg_6Sb_4BiBr_7$ have the same lattice constant and the same unit cell volume within the standard deviations. The chemical analyses and the method of preparation—there was no Bi present in the synthesis of $Hg_6Sb_5Br_7$ and chemical analyses gave certainly one atom of Bi per formula unit for $Hg_6Sb_4BiBr_7$—prove that the two compounds are of different composition. This indicates that the mercury–pnictogen framework is very rigid and determines the size of the unit cell. The small differences in the size of the hexabromo pnictides $[SbBr_6]^{3-}$ and $[BiBr_6]^{3-}$ do not have a significant effect on the lattice constant. This assumption is supported by the almost equal lattice constants of $(Hg_6As_4)[BiCl_6]Cl$ and the structurally closely related $(Hg_6As_4)[HgCl_6]Hg_{0.4}$ (12), which contains in the larger type of cavity of the Hg–As framework octahedral $[HgCl_6]^{4-}$ ions and in 40% of the smaller cavities of Hg atoms. Again, these two phases are undoubtly of different composition. The chemical composition is unequivocal for $Hg_6As_4BiCl_7$, and additionally we were able to reproduce the synthesis of $(Hg_6As_4)[HgCl_6]Hg_{0.4}$ from only mercury(I)chloride, mercury, and arsenic. We found diamagnetism and the refinement of the structure on single-crystal data gave, in contrast to (12), a slightly higher content of

Hg in the smaller cavity, leading to the formula $(Hg_6As_4)[HgCl_6]Hg_{0.6}$.

The discrete halide ions are located in the center of the cavities with no indication for positional disorder, and thus they have remarkably small displacement parameters (Fig. 1). The interactions between the two types of anions and the atoms of the surrounding cages are very weak. The shortest distances between the halide atoms of the octahedral complex anions and mercury atoms are 3.11 Å for the hexachloro and 3.33 Å for the hexabromo pnictides. The discrete halide ions are in first sphere linearly coordinated by As/Sb with an average As–Cl distance of 3.25 Å and an Sb–Br distance of 3.30 Å, and their second coordination sphere consists of six Hg atoms at an average distance of 3.34 Å to the chloride and 3.56 Å to the bromide ion.

In a recent publication, Shevelkov *et al.* described a cubic compound of composition $Hg_7Sb_4Br_6$ (13). This composition was derived from a structure refinement with Hg as the central atom of a $[HgBr_6]^{4-}$ unit only occupying its position by 70%. A Hg^{2+} ion was located in the second cavity, occupying its position by 30%. Hereby, the formula $(Hg_6Sb_4)[Hg_{0.7}Br_6][Hg_{0.3}]$ was derived. However 70% of the electrons of a Hg atom are 56, which is close to the 51 electrons of an Sb atom. When we refined the previously described model using our data of $Hg_6Sb_5Br_7$, we obtained residuals comparable with the undisordered model of the formula $Hg_6Sb_5Br_7$ ($wR(F_o^2) = 0.0841$, $R(F_o) = 0.0431$ for 666 F_o with $F_o^2 > 4\sigma$) and occupancies of 62% for Hg on position 4b and of 38% for Hg on position 4a. So we are able to reproduce the disordered structure model.

Our structural model for $Hg_6Sb_5Br_7$, however, needs no disorder or partial occupancies. Especially, the improbability of an incomplete occupancy of Hg being the central atom of a discrete $[HgBr_6]^{4-}$ group and the very close relationship to all other members of the $(Hg_6Y_4)[MX_6]X$ family justify our interpretation that "$Hg_7Sb_4Br_6$" might actually be identical with $Hg_6Sb_5Br_7$ described above. The chemical analysis supports our opinion. The observed Hg content of 0.526 is close to 0.507 for $Hg_6Sb_5Br_7$. A mercury content of 0.592 as expected for $Hg_7Sb_4Br_6$ was never observed, despite the analyses being complicated by an inevitable contamination of the samples by an amorphous colorless material that is probably a mixture of mercury bromides.

Recently we succeeded in synthesizing new members of the cubic structure family $(Hg_6Y_4)[MX_6]X$ with a formal substitution of the hexahalogeno pnictide anions against transition metal $[MX_6]^{3-}$ anions with $M = Mo^{3+}$, Ti^{3+} (24).

ACKNOWLEDGMENTS

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