

Synthesis and Structure of the Alkali–Metal Amalgams $A_3\text{Hg}_{20}$ ($A = \text{Rb}, \text{Cs}$), K_3Hg_{11} , $\text{Cs}_5\text{Hg}_{19}$, and $A_7\text{Hg}_{31}$ ($A = \text{K}, \text{Rb}$)

Evgeny Todorov and Slavi C. Sevov¹

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556

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The synthesis and single-crystal structures of four alkali–metal amalgams are reported. The compounds $A_3\text{Hg}_{20}$ ($A = \text{Rb}, \text{Cs}$) are of new structural type ($Pm\text{-}3n$, $Z=2$, $a = 10.737(1)$ Å and $10.913(1)$ Å, for $A = \text{Rb}$ and Cs , respectively), while K_3Hg_{11} is the first example of a mercury compound with the $\alpha\text{-La}_3\text{Al}_{11}$ -type structure ($Immm$, $Z=2$, $a = 5.122(1)$ Å, $b = 10.063(2)$ Å, $c = 14.782(3)$ Å). The structure of $A_7\text{Hg}_{31}$ ($A = \text{K}, \text{Rb}$) determined from single crystal ($P6/mmm$, $Z=1$, $a = 10.850(2)$ Å and $11.000(2)$ Å, $c = 10.210(2)$ Å and $10.377(3)$ Å, for $A = \text{K}$ and Rb , respectively) is compared with that of K_7Hg_{31} , previously known from powder diffraction only. $\text{Cs}_5\text{Hg}_{19}$ ($I4/m$, $Z=2$, $a = 11.803(3)$ Å, $c = 10.814(5)$ Å) is isostructural with the known $\text{Rb}_5\text{Hg}_{19}$. © 2000 Academic Press

INTRODUCTION

Among the most important physical and chemical properties of mercury is its ability to dissolve metals. It can be used as a meaning for their extraction and purification. The alloys that are formed, named amalgams, are often viscous liquids or ductile solids. However, depending on the nature of the other metal and its fraction in the amalgam, different compounds with defined stoichiometries and structures can be formed.

The alkali metals are among the few elements that are known to form crystalline intermetallic compounds with mercury. Some of their approximate chemical formulas were derived at the beginning of the century from thermal analyses (1). With the utilization of X-ray crystallography many structures of alkali–metal amalgams were solved and phase transitions and structural relations were studied (2). Currently, the number of structurally characterized $A\text{-Hg}$ compounds ($A = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$) is close to two dozen (Fig. 1). Here we report the synthesis and structure of the mercury-rich compounds $A_5\text{Hg}_{19}$, $A_3\text{Hg}_{20}$ ($A = \text{Rb}, \text{Cs}$),

K_3Hg_{11} , $A_7\text{Hg}_{31}$ ($A = \text{K}, \text{Rb}$). These systems were studied as side products of reactions designed to produce ternary phases of alkali–metals and elements of groups 12 and 14 (3).

EXPERIMENTAL SECTION

Synthesis

All compounds are air sensitive and decompose rapidly to elemental mercury and alkali–metal hydroxides. All operations were performed under inert atmosphere or vacuum. Details on the preparation and handling can be found elsewhere (3). The compounds were synthesized in high yields by heating stoichiometric mixtures of the elements (Alfa-Aesar) at 600°C for 3 to 10 h and slowly cooling them to room temperature ($5^\circ/\text{h}$). Often a few lines of other unidentified phases were present in the X-ray diffraction patterns. The compounds K_7Hg_{31} and $A_3\text{Hg}_{20}$ ($A = \text{Rb}, \text{Cs}$) were initially identified in the products of reactions loaded as $A\text{Hg}_5$. The interest toward this particular composition was based on possible analogies with the recently reported compounds ACd_{5+x} ($A = \text{Na}, \text{K}$) with channel or framework structures (4). A few crystals of the compound K_3Hg_{11} were initially found in the product of a reaction loaded as $\text{K}_8\text{Cd}_5\text{Hg}_{31}$. The same stoichiometry, $A_3\text{Hg}_{11}$, but with $A = \text{Cs}$ or Rb provided the compounds $\text{Cs}_5\text{Hg}_{19}$ and $\text{Rb}_5\text{Hg}_{19}$, respectively. Finally, the attempt to mix K and Rb in an amalgam with composition $\text{K}_{7/2}\text{Rb}_{7/2}\text{Hg}_{31}$ resulted in the synthesis of $\text{Rb}_7\text{Hg}_{31}$.

X-Ray Diffraction Studies

X-ray powder diffraction patterns of the reaction products were taken on an Enraf–Nonius Guinier camera with $\text{CuK}\alpha_1$ radiation and silicon as internal standard. Single crystals from all of the compounds were sealed in glass capillaries and used for diffraction data collection on CAD4 diffractometer with monochromated $\text{MoK}\alpha$ radiation, at room temperature. The structures were solved and refined

¹To whom correspondence should be addressed. E-mail: ssevov@nd.edu.

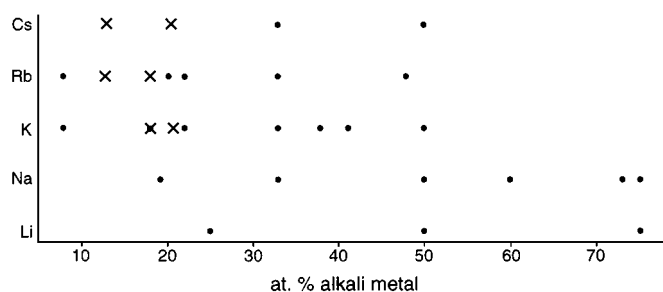
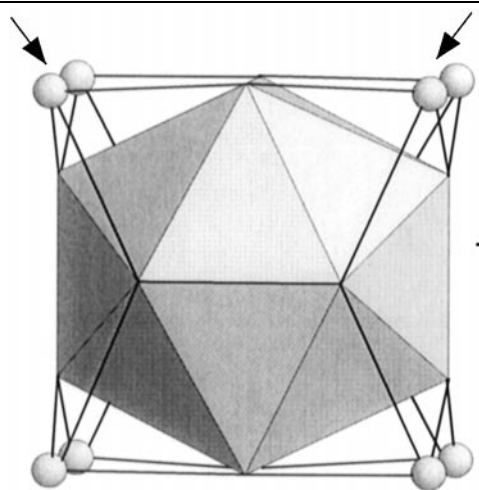
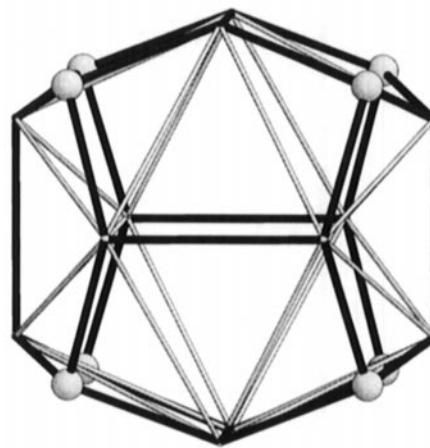


FIG. 1. Known compounds in the alkali-metal-mercury systems. The compounds reported in this work are marked with \times .

on F^2 with the SHELXTL-V5.0 package. Details on the data collection and refinement are listed in Table 1. The final residual factors are relatively high, most likely due to the significant absorption of mercury. Absorption corrections based on Ψ -scans were tried, but they were not always successful. The final positional and equivalent isotropic displacement parameters, anisotropic parameters, and important distances are listed in Tables 2, 3, and 4, respectively.



1



2

DESCRIPTION OF THE STRUCTURES

Only the compounds $A_3\text{Hg}_{20}$ are structurally novel. The structure of K_3Hg_{11} is new for an amalgam, but it belongs to the known $\alpha\text{-La}_3\text{Al}_{11}$ -type structure, which comprises numerous examples of intermetallic compounds, especially rear-earth alluminides (5). A review article by Dieseroth discusses the structure of K_7Hg_{31} (2a) derived from X-ray powder diffraction investigations. Our single-crystal studies on K_7Hg_{31} and $\text{Rb}_7\text{Hg}_{31}$, however, show some differences in the structure.

$A_3\text{Hg}_{20}$

The structure can be explained in two different ways—as built of linked octa-capped centered icosahedra of mercury, $\text{Hg}@\text{Hg}_{12}@\text{Hg}_8$ (1), or as related to the clathrate-I framework. In the first approach, the atoms Hg1 center icosahedra of 12 Hg2 atoms stacked in bcc lattice (Fig. 2). The icosahedron has the rare T_h point group symmetry with three pairs of opposing edges that are much shorter than the remaining 12 (2.855(9) vs 3.445(6) and 2.937(9) vs 3.451(5) Å for $A = \text{Rb}$ and Cs , respectively). The eight equilateral triangular faces are capped by Hg3 atoms resulting in a 20-atom polyhedron. The Hg3 atoms cap faces of two adjacent icosahedra and connect them. They can also be looked at as centers of trigonal prisms of six Hg2 atoms (D_{3h} symmetry) oriented along the body diagonals of the unit cell. The Hg4 atom is exobonded to Hg2 atoms of four different icosahedra with equal distances of 2.848(4) Å for $\text{Rb}_3\text{Hg}_{20}$ and 2.925(4) Å for $\text{Cs}_3\text{Hg}_{20}$. The geometry around it (point group D_{2d}) is somewhat distorted from ideal tetrahedral. The angles Hg2–Hg4–Hg2 have values of 101.24(8), 127.6(2) and 100.68(7), 129.0(2)° for the rubidium and cesium compounds, respectively.

An interesting comparison can be made between the structure of $A_3\text{Hg}_{20}$ and that of clathrate-I, X_4Y_{23} (6). Both crystallize in the space group $Pm\bar{3}n$ (223) and have five distinct atomic positions. The difference between the two is in the multiplicity of one position: Hg3 in $A_3\text{Hg}_{20}$ is at the $8e$ (1/4, 1/4, 1/4) position while it is replaced by a dimer of atoms at $16i$ (x, x, x) in the clathrate structure (Fig. 3). In other words, a dumbbell group in the clathrate structure is substituted by a single metal atom in $A_3\text{Hg}_{20}$ (the darker atoms in Fig. 2). The two fused building cages in the clathrate-I structure are a 20-atom polyhedron, a pyritohedron,

TABLE 1
Crystallographic Data for $A_x\text{Hg}_y$

Empirical formula	$\text{Rb}_3\text{Hg}_{20}$	$\text{Cs}_3\text{Hg}_{20}$	K_3Hg_{11}	$\text{Cs}_5\text{Hg}_{19}$	K_7Hg_{31}
Formula weight	8536.42	8821.06	2323.78	4475.74	6491.99
Space group, Z	$Pm\bar{3}n, 2$	$Pm\bar{3}n, 2$	$Im\bar{3}m, 2$	$I4/m, 2$	$P6/mmm, 1$
$a, \text{\AA}$	10.737(1)	10.913(1)	5.122(1)	11.803(3)	10.850(2)
$b, \text{\AA}$			10.063(2)		
$c, \text{\AA}$			14.782(3)	10.814(5)	10.210(2)
$V, \text{\AA}^3$	1237.7(2)	1299.7(3)	761.9(3)	1506.5(9)	1040.9(3)
$\rho_{\text{calcd}} (\text{g/cm}^3)$	11.453	11.27	10.129	9.867	10.356
$\mu (\text{mm}^{-1})$	129.3	121.7	111.1	102.3	114.5
$2\theta_{\text{max}} (\text{deg})$	50	50	50	50	40
h, k, l range	0/12, 0/12, 0/12	-12/12, 0/12, 0/12	-6/6, 0/11, 0/17	0/14, 0/14, 0/12	-10/10, 0/10, 0/9
Crystal size (mm)	$0.24 \times 0.14 \times 0.10$	$0.16 \times 0.14 \times 0.10$	$0.16 \times 0.12 \times 0.10$	$0.20 \times 0.12 \times 0.10$	$0.14 \times 0.12 \times 0.12$
Total/unique reflections	1285/220	2527/230	734/411	762/563	1118/234
Parameters	15	15	27	32	31
Goodness-of-fit on F^2	1.102	1.134	0.976	1.035	0.994
$R_1, wR_2 [I > 2\sigma_I]$ (%)	8.52, 22.16	7.15, 15.56	8.04, 17.96	6.56, 13.81	8.90, 18.16
R_1, wR_2 (all data)	14.97, 25.95	12.95, 18.09	12.97, 21.02	10.72, 15.76	16.08, 22.51
Max. min. $\Delta\rho$ ($e \text{\AA}^{-3}$)	3.88, -2.50	3.89, -5.07	4.65, -5.04	3.64, -2.68	3.14, -3.38

of 5^{12} type (the notation m^i shows the presence of i m -angular faces), and a 24-atom polyhedron of type $5^{12}6^2$. The corresponding two polyhedra in the structure of $A_3\text{Hg}_{20}$ are an icosahedron of type 3^{20} and a 20-atom polyhedron of $3^{12}4^86^2$ type, respectively. In fact, the pyritohedron can be described as originating from an octa-capped icosahedron in which the capping atoms are moved closer to the faces, **1** \rightarrow **2** (above). The result is a new anionic framework in which the atoms have a higher number of bonding interac-

tions. This is more or less expected since mercury has fewer electrons compared to the elements of group 14 that can form the clathrate-I structure.

Another significant difference between the clathrate-I structure and $A_3\text{Hg}_{20}$ is the type of atom on position $2a(0, 0, 0)$. While in the clathrate structure it is occupied by an alkali metal, in $A_3\text{Hg}_{20}$ a mercury atom, Hg1, is found at that position. Within the approximations of the extended-Hückel theory this Hg1 atom is with slightly positive charge of +0.3 while the rest of the mercury atoms have negative charges anywhere between -0.1 and -0.3. In other words, Hg1 can be viewed as electron-donating atom similar to the cations in the clathrate structures. Furthermore, this mercury atom provides additional orbitals for the framework bonding. Similar building units of centered icosahedra $Y@Y_{12}$ are known in the phases XY_{13} where X = alkali or alkaline-earth metal and Y = Cd, Zn, Be (7), but have not been observed in amalgams before. The compounds XY_{11} , among them KHg_{11} , are also related to the XY_{13} structure and contain building units of $Y@Y_{12}$ but these units are rather cuboctahedra and not icosahedra (2c). Empty icosahedra of Hg_{12} , on the other hand, have been recently characterized in $\text{K}_{29}\text{Hg}_{48}$ (2a).

$A_5\text{Hg}_{19}$ ($A = \text{Rb}, \text{Cs}$)

Two isostructural compounds were synthesized and structurally characterized by single-crystal studies. The structure of $\text{Rb}_5\text{Hg}_{19}$ has been described before. It can be related to the BaAl_4 -type structure in the following way (Fig. 4). The building unit in the structure of BaAl_4 is a bicapped truncated square prism, **3a**, with 18 vertices. If one of the edge dimers is condensed into an atom, a

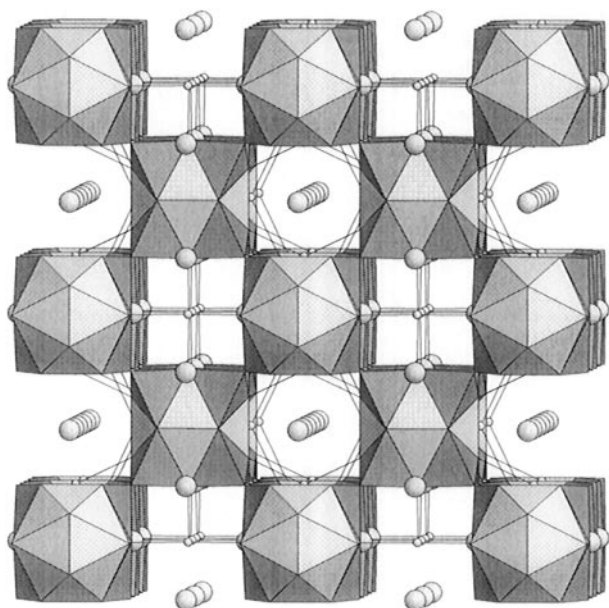
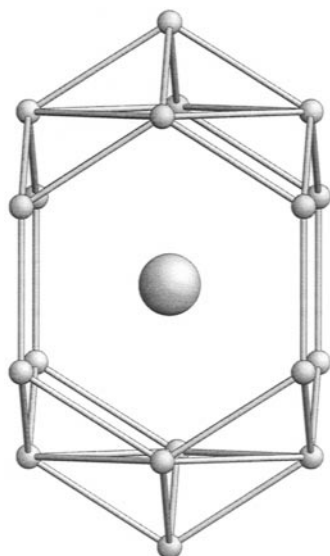
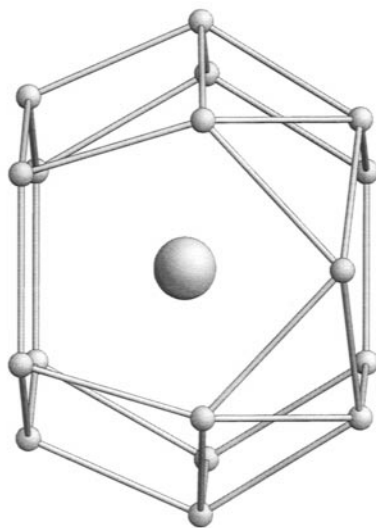
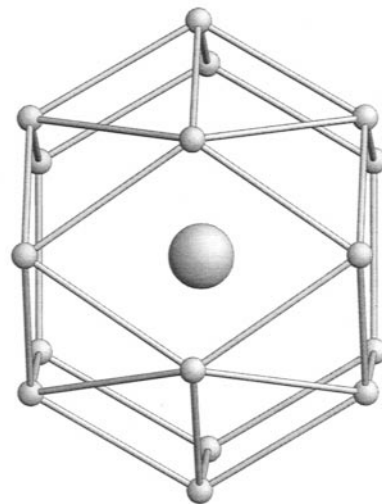


FIG. 2. The structure of $A_3\text{Hg}_{20}$ built of vertices sharing octa-capped centered icosahedra $\text{Hg}-\text{Hg}_{12}-\text{Hg}_8$. The four small bonded and the big spheres are atoms Hg4 and alkali-metal atoms, respectively.

polyhedron of 17 vertices is obtained, **3b**. The structure of A_5Hg_{19} is built of both 17- and 18-vertex polyhedra. The 18-atom polyhedra are linked only through their axial vertices and they form chains that are surrounded by the 17-vertex polyhedra. The formula of the compound can be represented as a defect $BaAl_4$, i.e., $A_5Hg_{19} = AHg_{4-x}$, where $x = 0.20$.

define which one is preferred (8). The compound K_3Hg_{11} provides not only the first example of an amalgam with the $\alpha-La_3Al_{11}$ structure but also the first one with alkali metal instead of rear-earth element. Therefore, it is with the largest cation that crystallize in this structural type since $r(K^+) = 1.52 \text{ \AA}$ while the corresponding radii of the rare-earths fall in the range from 1.00 to 1.17 \AA (9). Also, among the

**3a****3b****3c**

K_3Hg_{11}

The compound belongs to the $\alpha-La_3Al_{11}$ -type structure. This structural type includes primarily rear-earth compounds with aluminum and zinc (5, 8). The structure can be also related to the $BaAl_4$ -type structure as another defect version of the latter (Fig. 4), its formula can be rewritten as $K_3Hg_{(12-1)}$ or KHg_{4-x} where $x = 0.25$ (2b, 8). The building units in this structure can also be derived from the 18-vertex polyhedron, **3a**, found in $BaAl_4$. Instead of condensing one edge dimer of atoms that results in a 17-vertex unit as in A_5Hg_{19} , in this case two such edge dimers are condensed to form a 16-vertex polyhedron, **3c**. This and the original 18-vertex polyhedron are the building units in the structure of K_3Hg_{11} . The 18-vertex polyhedra share two opposite six-membered faces and the two axial atoms with four other polyhedra of the same kind and form layers. These layers are in turn separated by layers of the 16-atom vertex polyhedra.

Several factors, among which the size of the cation and the number of available electrons, are thought to influence the relative stability of the two structures, and therefore they

compounds with this structure, K_3Hg_{11} is the compound with the lowest electron count since its valence-electron concentration (VEC), i.e., the number of electrons per framework atom, is 2.27 while the corresponding numbers for the other isostructural compounds are in the range 2.82–3.82. Thus, the existence of K_3Hg_{11} establishes wider ranges for both the VEC and the cation size, where the structure type of $\alpha-La_3Al_{11}$ can be stable.

A_7Hg_{31}

The structure of K_7Hg_{31} was reported (2a) as a modified Ba_7Cd_{31} -type structure (10). It was solved and refined from X-ray powder diffraction data in space group $P6_3/mmc$ with doubled c axis with respect to the structure of Ba_7Cd_{31} , which crystallizes in $P6/mmm$. According to the authors, the structure of Ba_7Cd_{31} is perhaps not entirely correct. They suggest that a position that was originally refined as statistically disordered and with a half occupancy should be refined as an ordered position that alternates as full and vacant, and causes the doubling of the axis. In $P6/mmm$ this

TABLE 2
Positional and Equivalent Isotropic Displacement Parameters for $A_x\text{Hg}_y$

Atom		<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Rb₃Hg₂₀					
Hg(1)	2 <i>a</i>	0	0	0	0.062(4)
Hg(2)	24 <i>k</i>	0.2620(4)	0.1329(4)	0	0.066(2)
Hg(3)	8 <i>e</i>	1/4	1/4	1/4	0.051(2)
Hg(4)	6 <i>c</i>	1/4	0	1/2	0.075(3)
Rb	6 <i>d</i>	1/4	1/2	0	0.030(4)
Cs₃Hg₂₀					
Hg(1)	2 <i>a</i>	0	0	0	0.067(4)
Hg(2)	24 <i>k</i>	0.2584(4)	0.1341(4)	0	0.051(1)
Hg(3)	8 <i>e</i>	1/4	1/4	1/4	0.037(1)
Hg(4)	6 <i>c</i>	1/4	0	1/2	0.069(3)
Cs	6 <i>d</i>	1/4	1/2	0	0.025(2)
K₃Hg₁₁					
Hg(1)	8 <i>l</i>	0	0.2920(2)	0.1402(2)	0.0332(9)
Hg(2)	8 <i>l</i>	0	0.3559(2)	0.3410(2)	0.0321(9)
Hg(3)	4 <i>h</i>	0	0.8254(4)	1/2	0.050(2)
Hg(4)	2 <i>d</i>	1/2	0	1/2	0.084(4)
K(5)	2 <i>a</i>	0	0	0	0.034(8)
K(6)	4 <i>i</i>	0	0	0.709(1)	0.030(5)
Cs₅Hg₁₉					
Hg(1)	16 <i>i</i>	0.2027(2)	0.3852(2)	0.1394(2)	0.0378(7)
Hg(2)	4 <i>d</i>	0	1/2	1/4	0.036(1)
Hg(3)	16 <i>i</i>	0.0795(2)	0.1726(2)	0.2180(2)	0.0410(7)
Hg(4)	2 <i>a</i>	0	0	0	0.049(2)
Cs(1)	8 <i>h</i>	0.3254(3)	0.1191(4)	0	0.031(1)
Cs(2)	2 <i>b</i>	0	0	1/2	0.039(2)
K₇Hg₃₁					
Hg(1)	4 <i>h</i>	1/3	2/3	0.357(1)	0.047(4)
Hg(2)	6 <i>i</i>	1/2	0	0.1651(7)	0.060(4)
Hg(3)	6 <i>j</i>	0.2693(9)	0	0	0.071(4)
Hg(4)	6 <i>m</i>	0.105(1)	0.210(2)	1/2	0.18(2)
Hg(5)	12 <i>o</i>	0.1849(4)	0.3697(8)	0.2679(6)	0.067(3)
K(1)	2 <i>c</i>	1/3	2/3	0	0.08(3)
K(2)	2 <i>e</i>	0	0	0.210(8)	0.06(3)
K(3)	3 <i>g</i>	1/2	0	1/2	0.09(3)

position forms a hexagon (Fig. 5, bottom) with edges of 1.99(2) Å for the potassium and 2.54(4) Å for the rubidium compounds. When the site is half occupied these short distances are avoided by forming equilateral triangles (Fig. 5, middle) with two possible orientations and distances that are “normal” for Hg–Hg. The space group $P6_3/mmc$ and doubling of the *c* axis are achieved when the two orientations of the triangles alternate along the *c* axis for which there is no obvious reason.

We studied several single crystals from K_7Hg_{31} and $\text{Rb}_7\text{Hg}_{31}$ in a series of experiments. The cell assignment and particularly the correct choice of the *c* axis were checked with axial photographs of a few crystals from each compound. Data sets were collected with deliberately doubled *c* axis for both the potassium and rubidium compounds, and special attention was paid to the reflections with odd *l* since their observation would confirm or disprove the doubling. The highest intensity observed for a reflection with such odd *l* in the case of K_7Hg_{31} was 0.32σ . For $\text{Rb}_7\text{Hg}_{31}$ there was one peak with intensity 7σ and three other peaks with

TABLE 3
Anisotropic Displacement Parameters for $A_x\text{Hg}_y$

Atom	U11	U22	U33	U23	U13	U12
Rb₃Hg₂₀						
Hg(1)	0.062(4)	0.062(4)	0.062(4)	0	0	0
Hg(2)	0.081(3)	0.060(3)	0.056(3)	0	0	−0.007(3)
Hg(3)	0.051(2)	0.051(2)	0.051(2)	0.008(2)	0.008(2)	0.008(2)
Hg(4)	0.070(4)	0.086(8)	0.070(4)	0	0	0
Rb(5)	0.05(1)	0.022(5)	0.022(5)	0	0	0
Cs₃Hg₂₀						
Hg(1)	0.067(4)	0.067(4)	0.067(4)	0	0	0
Hg2	0.066(3)	0.050(3)	0.038(2)	0	0	0.001(2)
Hg(3)	0.037(1)	0.037(1)	0.037(1)	0.004(2)	0.004(2)	0.004(2)
Hg(4)	0.070(4)	0.067(6)	0.070(4)	0	0	0
Cs	0.018(3)	0.018(3)	0.038(6)	0	0	0
K₃Hg₁₁						
Hg(1)	0.033(2)	0.032(2)	0.035(2)	0.0012(8)	0	0
Hg(2)	0.030(2)	0.028(1)	0.038(2)	0.0033(8)	0	0
Hg(3)	0.061(4)	0.061(3)	0.028(2)	0	0	0
Hg(4)	0.14(1)	0.058(4)	0.053(4)	0	0	0
K(5)	0.04(2)	0.05(2)	0.02(1)	0	0	0
K(6)	0.04(1)	0.021(9)	0.03(1)	0	0	0
Cs₅Hg₁₉						
Hg(1)	0.038(1)	0.037(1)	0.038(1)	−0.0016(9)	0.0007(8)	0.0030(9)
Hg(2)	0.036(1)	0.036(1)	0.036(2)	0	0	0
Hg(3)	0.032(1)	0.043(1)	0.048(1)	0.006(1)	0.002(1)	0.0025(9)
Hg(4)	0.054(2)	0.054(2)	0.039(3)	0	0	0
Cs(1)	0.027(2)	0.036(2)	0.029(2)	0	0	0.002(2)
Cs(2)	0.041(3)	0.041(3)	0.034(5)	0	0	0
K₇Hg₃₁						
Hg(1)	0.046(5)	0.046(5)	0.039(6)	0	0	0.023(2)
Hg(2)	0.072(5)	0.077(7)	0.034(4)	0	0	0.038(4)
Hg(3)	0.074(6)	0.098(9)	0.049(5)	0	0	0.049(5)
Hg(4)	0.43(5)	0.02(1)	0.008(5)	0	0	0.011(6)
Hg(5)	0.062(4)	0.054(5)	0.084(4)	−0.018(5)	−0.009(2)	0.027(2)
K(1)	0.04(4)	0.04(4)	0.13(9)	0	0	0.02(2)
K(2)	0.07(4)	0.07(4)	0.08(7)	0	0	0.04(2)
K(3)	0.10(5)	0.01(4)	0.06(4)	0	0	0.00(2)

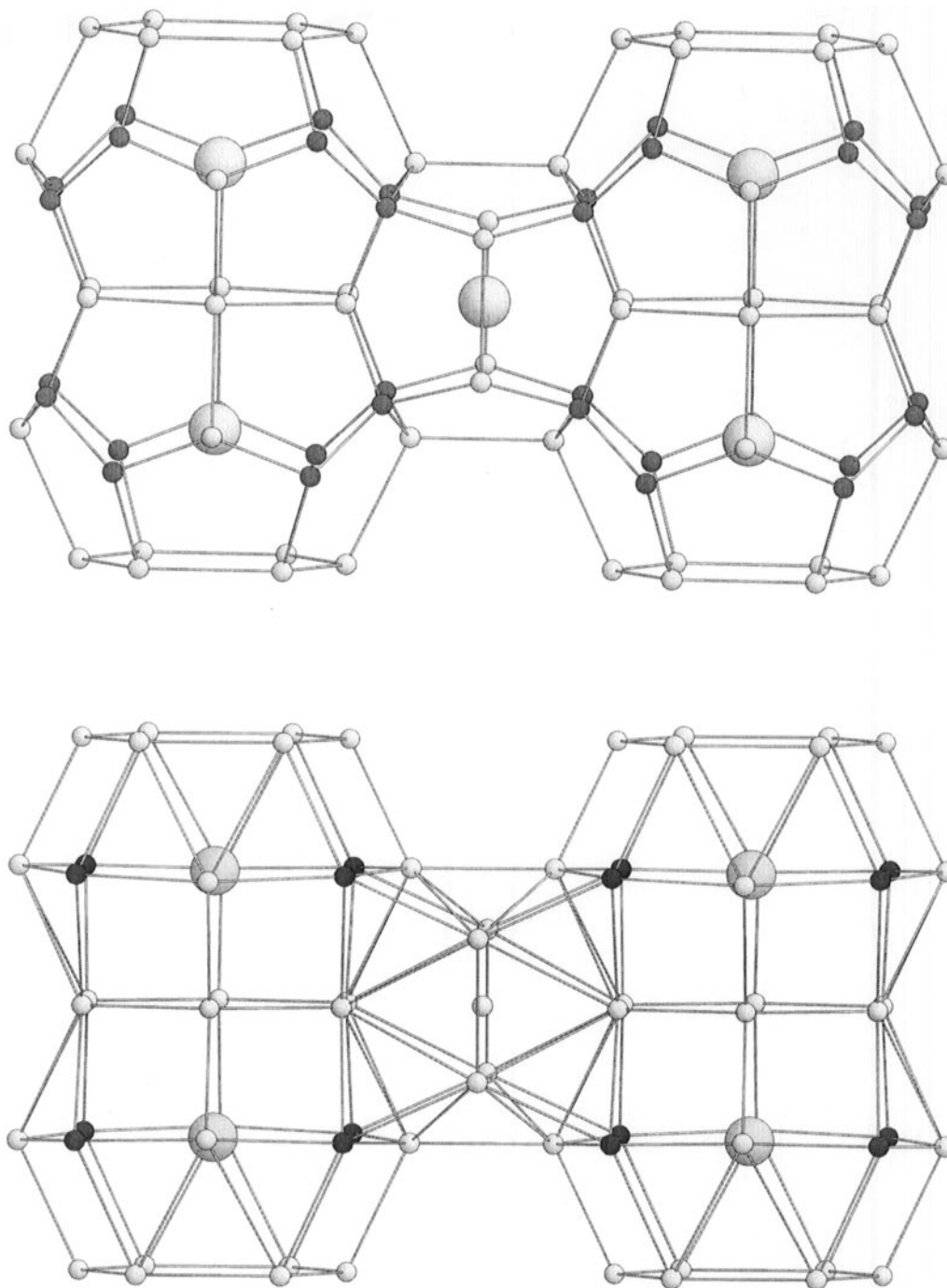


FIG. 3. (Top) Part of the clathrate-I type structure built from the two type cages: 20-atom pyritohedron (5^{12}) and the 24-atom polyhedron ($5^{12}6^2$). The atoms at position $16i$ are shown as darker spheres. If every couple of them is replaced by a single atom, the structure of A_3Hg_{20} (bottom) is obtained.

intensities in the range 1 to 3σ . They should be considered as sporadic events rather than regularities, especially when compared to the reflections with even l for which the intensities reach 4300σ . None of the axial photographs suggested doubling of the c axis either.

One of the building units in this structure is a 20-atom polyhedron. It shares three faces with its neighbors, thereby forming a layer of fused polyhedra. The formed hexagonal openings in the layers have the geometry of double "drums." Similar double drum units have been observed before, in

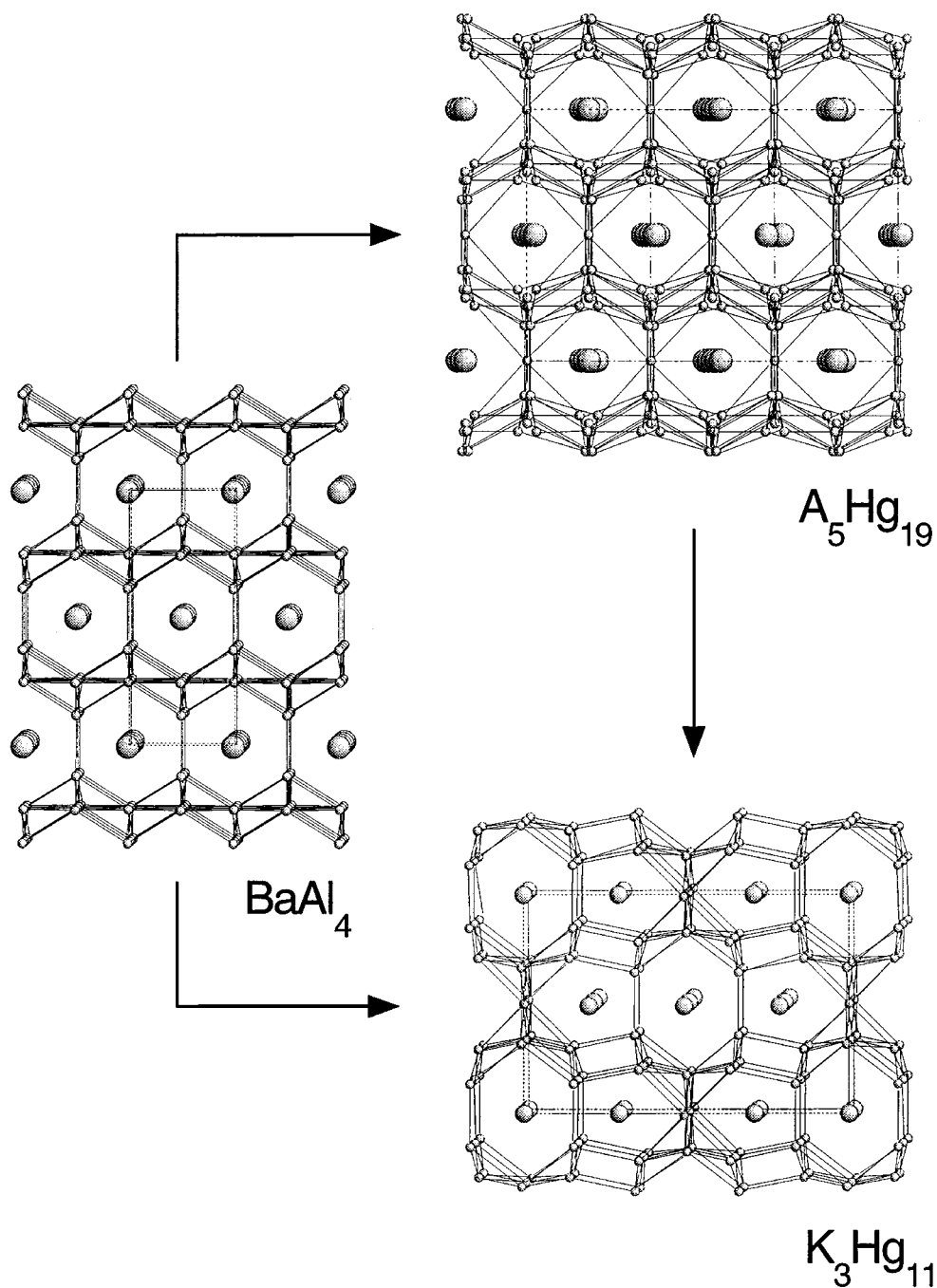


FIG. 4. The crystal structures of K_3Hg_{11} and A_5Hg_{19} ($A = Rb, Cs$) as related to the structure of $BaAl_4$. The difference between the three structures reflects the number of Hg-Hg bonds condensed to an atom.

$Na_8K_{23}Cd_{12}In_{48}$ and $KIn_{2-x}Cd_x$ (11). The two outer and the one inner hexagons in this structure are made of Hg5 and Hg3 atoms, respectively (Fig. 5). Each of the two drums is centered by an alkali atom situated closer to the outer faces, avoiding in this way both the short $A-A$ and $A-Hg_3$ distances (the inner hexagon is significantly smaller than the outer one).

In summary, the mercury-rich alkali-metal amalgams reported here illustrate the structural richness of these simple, binary systems. It is notable that this number and variety of structures exist in a relatively narrow stoichiometric window within the alkali-metal fractional interval of only 0.13 to 0.21.

TABLE 4
Important Interatomic Distances

		Rb ₃ Hg ₂₀	Cs ₃ Hg ₂₀		
Hg(1)–Hg(2)	12 ×	3.155(4)	3.178(4)		
Hg(2)–Hg(4)		2.848(4)	2.924(4)		
Hg(2)		2.854(9)	2.928(8)		
Hg(3)	2 ×	2.967(2)	3.008(2)		
Hg(1)		3.155(4)	3.178(4)		
Hg(2)	4 ×	3.446(5)	3.455(5)		
A		3.943(5)	3.994(4)		
A	2 ×	3.971(4)	4.067(3)		
Hg(3)–Hg(2)	6 ×	2.967(2)	3.008(2)		
A	3 ×	3.7960(4)	3.8583(5)		
Hg(4)–Hg(2)	4 ×	2.848(4)	2.924(4)		
A	4 ×	3.7960(4)	3.8583(5)		
A Hg(2)	4 ×	3.7960(4)	3.8583(5)		
Hg(3)	4 ×	3.7960(4)	3.8583(5)		
Hg(4)	4 ×	3.7960(4)	3.8583(5)		
Hg(2)	4 ×	3.943(5)	3.994(4)		
Hg(2)	4 ×	3.971(4)	4.067(3)		
		K ₃ Hg ₁₁			
Hg(1) Hg(4)		2.946(2)	Hg(1)	3.036(4)	
Hg(2)	2 ×	2.975(2)	Hg(3) Hg(2)	2 ×	2.976(4)
Hg(2)		3.036(4)	Hg(4)	2 ×	3.106(2)
Hg(3)	2 ×	3.312(2)	Hg(1)	4 ×	3.312(2)
Hg(2) Hg(2)		2.900(5)	Hg(4) Hg(1)	4 ×	2.946(2)
Hg(3)		2.976(4)	Hg(3)	4 ×	3.106(2)
Hg(1)	2 ×	2.975(2)			
		Cs ₅ Hg ₁₉			
Hg(1)–Hg(2)	1 ×	2.998(2)	Hg(4)	1 ×	3.254(3)
Hg(1)	1 ×	3.015(5)	Hg(2)	1 ×	3.991(2)
Hg(3)	1 ×	3.023(3)	Cs(1)	1 ×	3.782(4)
Hg(3)	1 ×	3.075(3)	Cs(2)	1 ×	3.785(2)
Hg(3)	1 ×	3.130(3)	Cs(1)	1 ×	3.793(4)
Cs(1)	1 ×	3.773(4)	Cs(1)	1 ×	4.074(4)
Cs(1)	1 ×	3.861(4)	Hg(4)–Hg(3)	8 ×	3.254(3)
Cs(1)	1 ×	3.914(3)	Cs(1)	4 ×	4.091(4)
Cs(2)	1 ×	4.052(2)	Cs(1)–Hg(2)	2 ×	3.678(3)
Cs(1)	1 ×	4.147(5)	Hg(1)	2 ×	3.773(4)
Hg(2)–Hg(1)	4 ×	2.998(2)	Hg(3)	2 ×	3.783(4)
Hg(3)	4 ×	3.991(2)	Hg(3)	2 ×	3.793(4)
Cs(1)	4 ×	3.678(3)	Hg(1)	2 ×	3.861(4)
Hg(3)–Hg(1)	1 ×	3.023(3)	Hg(1)	2 ×	3.914(3)
Hg(1)	1 ×	3.075(3)	Cs(2)–Hg(3)	8 ×	3.785(2)
Hg(1)	1 ×	3.130(3)	Hg(1)	4 ×	4.052(2)
Hg(3)	2 ×	3.172(3)			
		K ₇ Hg ₃₁			
Hg(1)–Hg(1)	2.92(2)	K(1)	2 ×	3.557(4)	
Hg(5)	3 ×	2.934(8)	Hg(3)–Hg(3)	2 ×	2.92(1)
K(3)	3 ×	3.457(4)	Hg(2)	2 ×	3.018(9)
K(1)		3.643(10)	Hg(5)	4 ×	3.241(5)
Hg(2)–Hg(3)	2 ×	3.018(9)	K(2)	2 ×	3.62(5)
Hg(5)	4 ×	3.155(4)	K(1)	2 ×	4.009(6)
Hg(2)		3.37(2)	Hg(4)–Hg(4)	2 ×	1.98(2)
K(3)		3.419(8)	Hg(5)	2 ×	2.80(1)
Hg(4)	2 ×	3.42(4)			
K(2)	2 ×	3.56(7)			
K(3)	2 ×	3.84(2)			
Hg(5)–Hg(4)		2.80(1)			
Hg(2)	2 ×	3.155(4)			
Hg(3)	2 ×	3.241(5)			
Hg(5)	2 ×	3.474(8)			
K(2)		3.53(2)			
K(3)	2 ×	3.804(4)			
K(1)		3.907(7)			

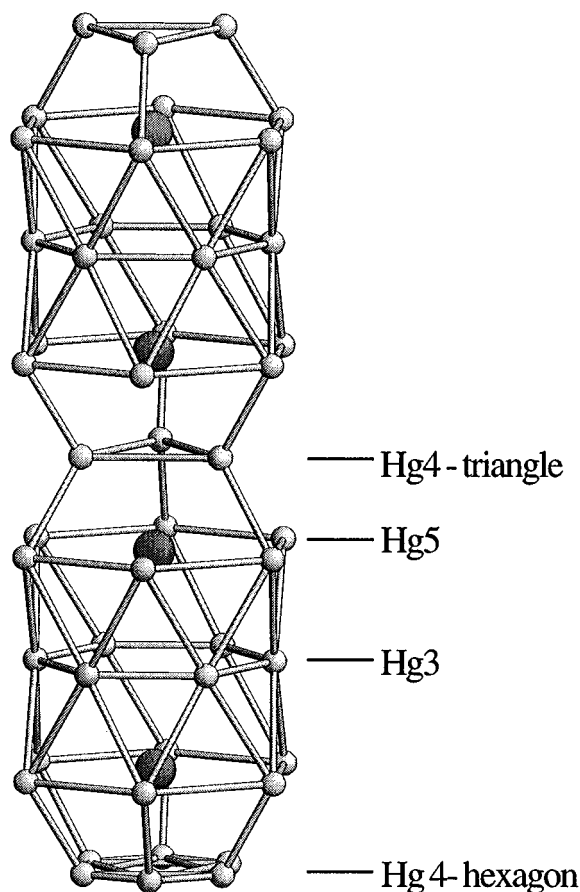


FIG. 5. Part of the infinite chain in *A*₇Hg₃₁. The hexagonal openings of the layers formed by fused 20-atoms polyhedra have the geometry of double drums with two alkali atoms close to the outer faces. These are connected to hexagons of atoms Hg4. Since the latter are 50% occupied they are more correctly described as triangles.

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