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A_4Ge_9 (A = K, Rb) as Precursors for Hg-Substituted Clathrate-I Synthesis: Crystal Structure of $A_8Hg_3Ge_{43}$

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The Hg-substituted type-I clathrates $A_8Hg_{3+x}Ge_{43-x}$ (A = K, Rb) were obtained by solid-state reactions from the corresponding Zintl phases A_4Ge_9 and Hg or HgO. The crystal structures of the compounds were determined by single-crystal and powder X-ray diffraction methods. They crystallize in the space group $Pm\bar{3}n$, with a = 10.849(1) Å and x = 0.19(5) for $K_8Hg_{3+x}Ge_{43-x}$ (**1**) and a = 10.875(1) Å and x = 0.03(7) for $Rb_8Hg_{3+x}Ge_{43-x}$ (**2**). Specific atomic positions (6*c* site) of the Ge framework are partially substituted by Hg atoms, whereas the alkali-metal atoms reside at the center of the cavities. Both compounds exceed the electron-counting rule for Zintl phases.

Introduction

Polyanionic clathrates of the elements Si, Ge and Sn have been studied for over 40 years.[1] The interest in these compounds, however, rose rapidly in the last decade, since some ternary compounds, such as $Sr_8Ga_{16}Ge_{30}$,[2] exhibit considerable thermoelectric efficiency. This perspective becomes even more intriguing for certain doped clathrates that may act as Kondo insulators.[3] In this light, synthetic approaches of chemically well-defined materials are necessary. Different synthetic approaches have been applied, depending mostly on the properties of the tetrel element.[4,5] Sn-based clathrates are predominantly obtained by fusion of the elements at temperatures below 700 °C.[1,5] Because of the much higher melting points of the elements, the synthesis of Si and Ge clathrates requires reaction temperatures around 1000 °C or even higher as well as application of external pressure.[5] Alternatively, thermal decomposition of A_4Tt_4 phases (Tt = Si, Ge) under dynamic vacuum, in order to remove the excess alkali metal, has been implemented for the synthesis of type-I A_8Tt_{46} and type-II $A_{24-x}Tt_{136}$ clathrates (A = Na, K, Rb, Cs).[6] Recently, high yields of crystalline $A_{8-x}Si_{46}$ (A = Na, K) were achieved by the oxidation of A_4Si_4 with gaseous HCl or H_2O,[7] whereas the guest-free type-II $\square_{24}Ge_{136}$ clathrate (□ denotes here vacant cationic position) was synthesized by heating Na_4Ge_9 to 300 °C in a 1:1 mixture of $AlCl_3$ and *n*-dodecyltrimethylammonium chloride.[8] Moreover, the type-IX clathrate Ba_6Ge_{25} was found to produce type-I $Ba_8Cu_{6-x}Ge_{40+x}$ in rather high purity when reacted with stoichiometric amounts of Cu and Ge.[9]

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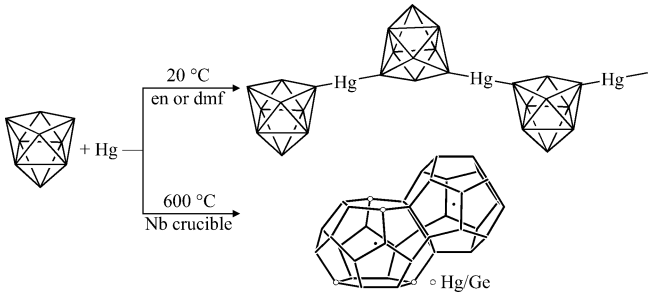
Recently we reported on the synthesis of Hg-substituted clathrates $A_8Hg_4Sn_{42}$ (A = K, Rb, Cs).[10] All attempts to prepare the homologous Ge clathrates as pure phases failed mainly because of the high melting temperature of Ge. Motivated by our successful reaction of $[Ge_9]^{4-}$ clusters with Hg in ethylenediamine (en) or dimethylformamide (dmf) solutions leading to the isolation of the polymer $^1_\infty[HgGe_9]^{2-}$ (Scheme 1),[11] we performed the synthesis of the Hg-substituted type-I clathrates $A_8Hg_{3+x}Ge_{43-x}$ using the neat solid A_4Ge_9 (A = K, Rb) as precursor.



Scheme 1. Reaction of $[Ge_9]^{4-}$ with Hg, towards formation of the polymer $^1_\infty[HgGe_9]^{2-}$ or the clathrate-I $A_8Hg_3Ge_{43}$ (A = K, Rb).

Results and Discussion

Syntheses

Initially, the binary phases A_4Ge_9 (A = K, Rb) were obtained in corundum crucibles.[12] Two different routes were then followed for the synthesis of the clathrates. Equimolar amounts of A_4Ge_9 and Hg were loaded in Nb ampoules. These were weld-sealed, enclosed in fused silica tubes, heated to 600 °C for 24 h, annealed at 400 °C for 72 h, and subsequently cooled down to room temperature at a rate of

4 K min^{-1}. The products consisted of a microcrystalline powder of $A_8Hg_{3+x}Ge_{43-x}$ and a secondary phase whose powder pattern remains unindexed. This admixture proved to be air sensitive and reacted exothermally with distilled water and acetone. Some Hg drops were also observed and were removed under dynamic vacuum (12 h at 100 °C and 2×10^{-2} mbar). The powder diagrams of the resulting pure phases of $A_8Hg_{3+x}Ge_{43-x}$ were analyzed with the Rietveld method. It seemed crucial to use deficient amounts of A_4Ge_9, because α-Ge − which was formed as byproduct otherwise − was difficult to remove.

In search of a method to also obtain single crystals of $A_8Hg_{3+x}Ge_{43-x}$, various flux methods and reaction mixtures were checked. Finally, a mixture of $A_4Ge_9/WO_3/HgO$ was successful. This was loaded, in a molar ratio of 5:6:3, in a Nb ampoule and treated thermally exactly as described for the first method. The reaction products consisted of grey, good-quality single crystals of $A_8Hg_{3+x}Ge_{43-x}$ as well as significant amounts of A_2WO_4 and α-Ge, according to the X-ray powder diffraction (XRPD) analysis. The silver-grey single crystals were checked with energy-dispersive X-ray analysis (EDX) for the absence of W and then measured on the diffractometer. HgO decomposes already at 400–450 °C allowing Hg to react with Ge, in its "activated" A_4Ge_9 form. The presence of WO_3 or eventually A_2WO_4 presumably favors the crystal growth of the clathrate, as recently found for K_4Ge_9.[13] Noteworthy, attempts to synthesize the title compounds by fusion of the pure elements were rather unsuccessful. The substantial vapor pressure of Hg at high temperatures triggered the swelling of the ampoule until it cleaved, leading to the escape of Hg and alkali metals from the ampoule. Only the reaction of A and Ge (or $A_8Ge_{44}\square_2$[14]) with an excess of Hg at 700 °C for 15 d resulted in $A_8Hg_{3+x}Ge_{43-x}$, but in yields below 10%, as indicated by the quantitative analysis of the corresponding powder.

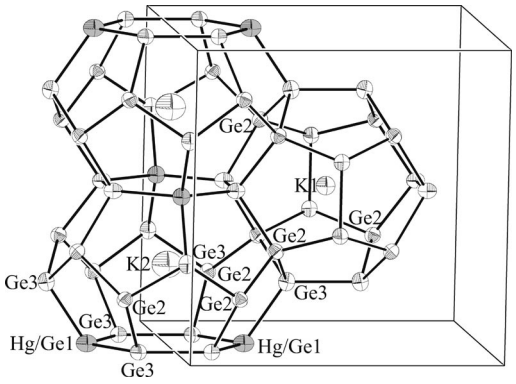


Figure 1. Partial view of the clathrate-I structure for $K_8Hg_{3.19}Ge_{42.81}$: two types of framework cages in the unit cell centered by the guest metal [K1@Ge_{20} and K2@(Ge/Hg)$_{24}$]. All thermal ellipsoids are presented at 90% probability level.

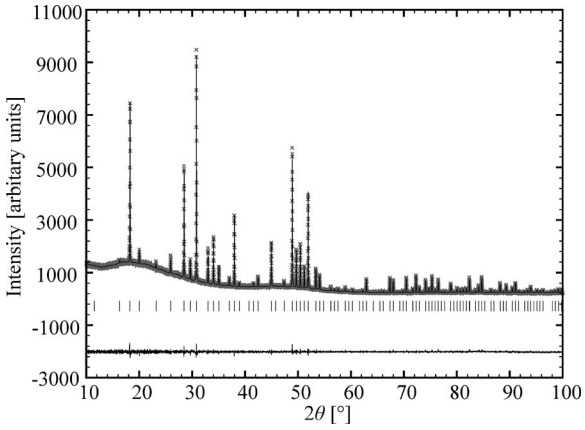


Figure 2. X-ray powder diagram (×) and theoretical pattern (solid line) for $K_8Hg_{3.37(3)}Ge_{42.63(3)}$. The vertical lines represent the Bragg positions. The difference between the observed and the theoretical pattern is shown below.

Crystal-Structure Analysis

The compounds $A_8Hg_{3+x}Ge_{43-x}$ possess a clathrate-I structure (Figure 1) with primitive cubic lattice. The crystallographic sites of the four-bonded framework atoms are 6*c*, 16*i* and 24*k*, and those of the guest atoms are 2*a* and 6*d*. All sites are fully occupied; however, the 6*c* site has a mixed occupation of Hg and Ge. According to the single-crystal analysis, *x* equals to 0.19(5) for $K_8Hg_{3+x}Ge_{43-x}$ and to 0.03(7) for $Rb_8Hg_{3+x}Ge_{43-x}$. The composition of the powder products was refined as $K_8Hg_{3.37(3)}Ge_{42.63(3)}$ (Figure 2) and $Rb_8Hg_{3.43(3)}Ge_{42.57(3)}$ (see also Supporting Information). Within the accuracy of the two methods, the composition of the clathrates is approximately $A_8Hg_3Ge_{43}$. There are no indications of a superstructure as has been observed for the binary phases $A_8Sn_{44}\square_2$ (A = Rb, Cs).[15]

As expected, the Hg/Ge–Ge bonds are slightly longer than the Ge–Ge bonds. Moreover, $Rb_8Hg_{3.03}Ge_{42.97}$ shows a small increase of all interatomic distances compared to $K_8Hg_{3.19}Ge_{42.81}$, because of the different radii of the alkali metals [*d*(Hg/Ge–Ge) = 2.5634(8) Å and average *d*(Ge–Ge) = 2.503(1) Å for **1**, whereas *d*(Hg/Ge–Ge) = 2.564(2) Å and average *d*(Ge–Ge) = 2.511(2) Å for **2**]. Both compounds exhibit anisotropy in the displacement parameters of the Hg/Ge1 site. The U_{22} value is significantly larger than U_{11} and U_{33}. The same effect was recently observed for $A_8Hg_4Sn_{42}$ (A = K, Rb, Cs).[10] It seems trivial to assess the origin of this anisotropy, since the bond-length difference between Ge–Ge and Hg–Ge should reasonably affect mostly the displacement of the Ge3 position, which is adjacent to the mixed occupied Hg/Ge1 site, and not vice versa. Note also that the Hg–Ge bond lengths are similar to the values of 2.54–2.61 Å and 2.55 Å found for [K([2.2.2]-crypt)]$_2$-[$HgGe_9$](en)$_2$ and [K([2.2]-crypt)]$_2$[$HgGe_9$](dmf), respectively.[11]

According to the 8-N rule, the conduction band of $A_8Hg_3Ge_{43}$ is occupied with 2 electrons and, interestingly, the Ge–Ge bond lengths in **1** and **2** are slightly, but significantly, larger than those in α-Ge (*d* = 2.445 Å) and K_8Ge_{44} (average *d* = 2.471 Å).[14] The class of known ternary germanium clathrates shows, in principle, atom mixing on all three framework sites as observed for the triel-rich com-

Table 1. Crystal and structure refinement parameters for **1** and **2**.

Chemical formula	$K_8Hg_{3.19}Ge_{42.81(5)}$ (**1**)	$Rb_8Hg_{3.03}Ge_{42.97(7)}$ (**2**)
Space group (No.)	$Pm\bar{3}n$ (223)	$Pm\bar{3}n$ (223)
Formula weight	4060.26	4410.74
Temperature, T [°C]	20	20
Radiation, λ [Å]	Mo-K_α, 0.71073	Mo-K_α, 0.71073
Z	1	1
$\rho_{calcd.}$ [g cm^{-3}]	5.280	5.695
a [Å]	10.849(1)	10.875(1)
V [Å^3]	1276.9(3)	1286.1(3)
Absorption coeff., μ [mm^{-1}]	34.94	41.18
F (000)	1777	1913
θ range for data collection [°]	4.20–27.82	4.19–27.75
Reflections collected	10100	10214
Independent reflections	288 (R_{int} = 0.109)	298 (R_{int} = 0.095)
Parameters	17	17
Goodness-of-fit on F^2	1.093[a]	1.125[a]
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.028, wR_2 = 0.074	R_1 = 0.031, wR_2 = 0.078
R indices (all data)	R_1 = 0.037, wR_2 = 0.079	R_1 = 0.045, wR_2 = 0.089
Largest diff. peak and hole [e Å^{-3}]	1.499 and –1.266	1.893 and –2.571

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{[\Sigma w[(F_o)^2 - (F_c)^2]^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$; $w = [\sigma^2(F_o)^2 + (aP)^2] - 1$, where $P = [(F_o)^2 + 2(F_c)^2]/3$ and a = 0.039 for both compounds.

pounds $Ae_8Ga_{16}Ge_{30}$ (Ae = Sr, Ba).[2,16] Mixed positions on only two sites are discussed for $A_8Tr_8Ge_{38}$ (A = K, Rb, Cs and Tr = Al, Ga, In)[17] and $Ba_8M_8Ge_{38}$ (M = Zn, Cd),[18] whereas in compounds with smaller amounts of dopants, such as $Ba_8M_6Ge_{40}$ (M = Cu, Ag, Au),[19] $K_8Zn_4Ge_{42}$[20] and the here presented $A_8Hg_3Ge_{43}$ (A = K, Rb), only one crystallographic site is statistically occupied by two atom types. Beside the title compounds, all ternary phases fulfil the 8-N rule, while $A_8Hg_3Ge_{43}$ is electron-rich and follows the trend of the binary phases $A_{8-x}Si_{46}$ (A = Na, K, Ba) and $Ba_8Ge_{43}\square_3$.[5]

Conclusions

The title compounds represent the first mercury-substituted germanium clathrates. Their synthesis did not follow the usual straightforward route of fusing the elements. Instead, the cluster compounds A_4Ge_9 were used as precursors so that the clathrate is formed in high yields at temperatures that do not exceed 600 °C. Unlike their Sn homologous $A_8Hg_4Sn_{42}$[10] and many other ternary Ge clathrates, these new compounds exceed the electron-counting rule for Zintl phases by having approximately 2 electrons in the conduction band.

Experimental Section

Synthesis: The manipulations were carried out in an Ar-filled glove box. Starting materials: K (Merck, 99%), Rb (Riedel de Haën, 99.9%), Ge (Chempur, 99.9999%+), Hg (Aldrich, 99.99%+), HgO (Alfa Aesar, 99%) and WO_3 (Aldrich, 20 μm powder, 99%+).

X-ray Powder Diffraction: The phase analysis of the homogenized reaction products was performed with a Stoe STADI P2 diffractometer [Ge(111) monochromator for Cu-K_α radiation] equipped with a linear position-sensitive detector. The powder patterns were refined with the Rietveld method.[21]

Single-Crystal X-ray Diffraction: The crystals were mounted on the Oxford Xcalibur3 diffractometer equipped with a CCD detector. Full data collections at room temperature included four series of 138 frames with 30-s exposure time and a crystal-detector distance of 50 mm. The reflections were collected over the range $2\theta_{max}$ = 55.5° and corrected numerically for absorption using the program X-Shape.[22] The data were processed using the SHELXTL package and solved by direct methods (Table 1).[23] Further details of the crystal-structure investigations can be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-mail: crysdata@fiz-karlsruhe.de) on quoting the depository numbers CSD-418045 (**1**) and -417502 (**2**).

EDX Analyses: These were carried out for single crystals by using a JEOL 5900LV scanning electron microscope system operating at 20 kV and equipped with a LINK AN 10000 detector system.

Supporting Information (see footnote on the first page of this article): ORTEP view of **1** and **2**, tables of atomic coordinates, bond lengths, anisotropic displacement parameters, and Rietveld analyses of the powder diagrams are available.

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