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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication
pubs.acs.org/JACS

Tin Clathrates with the Type II Structure

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S Supporting Information

ABSTRACT: For a very long time, $Ba_{16}Ga_{32}Sn_{104}$ has been the sole representative of tin clathrates with the type II structure. Herein, we present several new members of this structural family: $Cs_8Ba_{16}Ga_{39.7(3)}Sn_{96.3(3)}$, $Rb_{9.9(5)}Ba_{13.3(2)}Ga_{36.4(3)}Sn_{99.6(3)}$, and $K_{2.0(4)}Ba_{14.0(4)}Ga_{30.4(2)}Sn_{105.6(4)}$. The successful synthesis of these novel compounds was facilitated through the use of alkali and alkaline-earth metals, which selectively fill the available cages.

Inorganic clathrates based on the group 14 elements Si, Ge, and Sn have been known for close to 50 years already.[1] Their potential for optical, thermoelectric, and other valuable applications, however, has become a point of interest only in more recent years.[2] Such materials boast open-framework structures with large cages, and in analogy with the gas hydrates $G_8(H_2O)_{46}$ and $G_{24}(H_2O)_{136}$ (G = Xe, Cl_2, CH_4, etc.),[3] they are classified with different structure types: types I and II being the most common ones.[4,5] Type I clathrates have the general formula A_8Tt_{46}, where A denotes the guest atoms in the resulting cages (alkali, alkaline-earth metals and europium), and Tt = Si, Ge, Sn as framework atoms. The latter can be partially substituted with elements from groups 13, 12, and even late transition metals from groups 11 and 10 (E), accounting for ~150 different $A_8(E,Tt)_{46}$ representatives.[4] On the contrary, type II compounds are rarer with only about 25 known examples.[4] Type II compounds have the rather complex general formula $A_{24-x}Tt_{136}$ ($0 \leq x \leq 24$) with compositions varying from the guest-free structures Si_{136}[6] and Ge_{136},[7] to $Na_{24-x}Si_{136}$,[8] to quaternary phases, such as $Cs_8Na_{16}Ga_{21}Si_{115}$,[9] $Rb_{7.3}Na_{16}Ga_{20}Si_{116}$,[9] $Cs_8Na_{16}Ag_{6.7}Ge_{129.3}$,[10] and $Cs_8Na_{16}Cu_5Ge_{131}$.[11] For a long time, the only representative of the type II structure among the tin clathrates has been $Ba_{16}Ga_{32}Sn_{104}$, where only the small cages are filled with Ba atoms and the large ones are empty.[12] Interestingly, the synthesis of this compound had been achieved from a reaction with small amounts of additional potassium metal as a starting material; however, its possible inclusion in the crystal structure has remained an open question until today. With the present communication we unequivocally address this long-standing issue by detailing our investigations of the systems A−Ba−Ga−Sn (A = Na, K, Rb, and Cs). Our studies yielded the first-of-a-kind clathrate with type II structure, $Cs_8Ba_{16}Ga_{40}Sn_{96}$, which represents the only confirmed type II clathrate of tin, where both cages are completely filled by two types of guest atoms. We present the synthesis, structure, and bonding of this material as well as the structural characterization of the Rb and K analogs. Also, briefly discussed is the re-evaluation of the $Ba_{16}Ga_{32}Sn_{104}$ structure[12] and the recently reported type II clathrate $K_{8+x}Ba_{16-x}Ga_{40-y}Sn_{96-z}\square_{y+z}$ ($\square$: vacancy).[13]

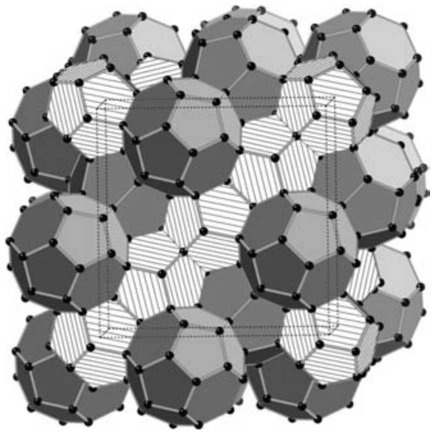

Figure 1. View of the polyanionic framework in type II clathrates (pentagonal dodecahedra: light-gray, crossed; hexakaidecahedra: dark-gray shaded).

Type II clathrates crystallize in the cubic space group $Fd\bar{3}m$ (no. 227). The open framework of this structure (see Figure 1) comprises 136 tetrahedrally coordinated atoms per unit cell. In the case of the title compounds, the framework is made of statistically disordered Ga and Sn atoms on all three different Wyckoff sites: 96*g*, 32*e*, and 8*a*. There are two different kinds of cages, offering space for a total of 24 guest atoms: 16 pentagonal dodecahedra (5^{12}) and 8 hexakaidecahedra ($5^{12}6^4$).[14] The centers of these polyhedra are Wyckoff sites 16*c* and 8*b*, respectively. The larger 28 atom polyhedra share their four hexagonal faces in a fashion that resembles the diamond structure. The smaller 20 atom polyhedra are arranged in layers, stacked along the body diagonal of the cubic cell in ABC sequence. One could also view the structure as an arrangement of supertetrahedra made up of fused pentagonal dodecahedra (5^{12}), in whose center a hexakaidecahedron ($5^{12}6^4$) is located. The large size difference between the (5^{12}) and the ($5^{12}6^4$) polyhedra has been cited as the critical element for the formation of the first clathrate II compounds with full occupation of all cages, $(Cs\text{ or }Rb)_8Na_{16}(Si\text{ or }Ge)_{136}$;[15] the structure has been suggested to prefer two very different "fillers" that match well with the sizes of the available cages. The same realization can also explain the full occupation of the small cavities by Ba atoms in the $Ba_{16}Ga_{32}Sn_{104}$ structure,[12] while the large ones remain empty. To fill them,

Received: November 20, 2012
Published: January 17, 2013

we reasoned, a larger atom will be required, and by using Cs in combination with Ba atoms, we were able to obtain the sought after $Cs_8Ba_{16}Ga_{40}Sn_{96}$, where Cs and Ba are filled in the ($5^{12}6^4$) and the (5^{12}) cages, respectively. Further discussion on these important traits follows.

Aiming at full understanding of the effects of the "filler" atom size, along with the charge balance requirements for a Zintl phase, we synthesized four clathrate II compounds with refined chemical formulas $Cs_8Ba_{16}Ga_{39.7(3)}Sn_{96.3(3)}$ (**1**), $Rb_{9.9(5)}Ba_{13.3(2)}Ga_{36.4(3)}Sn_{99.6(3)}$ (**2**), $K_{2.0(4)}Ba_{14.0(4)}Ga_{30.4(2)}Sn_{105.6(4)}$ (**3**), and $Ba_{16}Ga_{32.1(3)}Sn_{103.9(3)}$ (**4**). The chemical makeup of the four phases was also independently established by means of energy dispersive X-ray (EDX) spectroscopy (see Supporting Information, SI). A closer inspection of the lattice parameters immediately reveals something out of the ordinary: a = 17.0283(5) Å for **1**, a = 17.0367(5) Å for **2**, a = 17.0292(6) Å for **3**, and a = 16.9963(15) Å for **4**. Although not by much, the unit cell volume of the Cs compound is smaller than the volumes of both the Rb and K representatives. Such observation seemingly contradicts the expected lattice expansion, as the larger alkali atoms are accommodated within the structure. The likely explanation for this can be traced to the fact that the alkali metal occupations vary (as well as the Ga:Sn ratios), suggesting that there are competing effects necessitating a careful examination.

First, let us closely examine the structure of the Cs-containing compound **1**. Here, the Cs atoms are very large and fit especially well inside the larger hexakaidecahedra, whereas the smaller Ba atoms fit better in the pentagonal dodecahedra. Refinements of the structure indicate a complete occupation and order in both cavities. All three framework sites are statistically mixed occupied by Sn and Ga atoms with different preferences of substitution in the framework positions resulting in Sn:Ga ratios of approximately 67:33 on site 96*g*, 86:14 on site 32*e*, and 55:45 on site 8*a*. The final formula is in excellent agreement with the Zintl–Klemm rules,[16] since the 40 valence electrons from the 16 Ba^{2+} and 8 Cs^+ cations are required by the 40 Ga atoms in order to satisfy their octets according to $[Cs^+]_8[Ba^{2+}]_{16}[4b\text{-}Ga^{1-}]_{40}[4b\text{-}Sn^0]_{96}$ (4*b* denotes an atom in a tetrahedral coordination), i.e., the material should be a semiconductor.

The occupation of the cages in compound **3** is starkly different. The combination of almost same-sized Ba and K[17] results in guest-free $(Ga,Sn)_{28}$, whereas the $(Ga,Sn)_{20}$ cages are mixed occupied. The refined Ba:K ratio is ~7:1. As there are 8 fewer cations (in total), it is understandable that the Ga substitution in the framework decreases compared with **1**, which is evident in the ratio of Sn:Ga = 71:29 on site 96*g*, 69:31 on site 8*a* and only Sn atoms on site 32*e*, respectively. The final formula again satisfies the Zintl–Klemm rules according to $[K^+]_2[Ba^{2+}]_{14}[4b\text{-}Ga^{1-}]_{30}[4b\text{-}Sn^0]_{106}$.

In compound **2**, both types of "filler" atoms are different in size,[17] but the size differential is not as significant as it is between Cs and Ba. Thus, it can be easily understood why the refinements suggest mixed occupation in both cages with the following caveats: the $(Ga,Sn)_{20}$ cages, as discussed above, favor the smaller Ba atoms with an admixture of Rb–Ba:Rb ratio is 83:17. The oversized $(Ga,Sn)_{28}$ polyhedra, however, encapsulate only the larger Rb^+ cations. Noteworthy, because the Rb atoms are not sufficiently big and do not fit well inside the $(Ga,Sn)_{28}$ cages, the refinements suggest that they are displaced (Figure 2) from the geometric center corresponding to the site 8*b* ($^3/_8$, $^3/_8$, $^3/_8$). The disorder was modeled by allowing the Rb to reside at site 96*g* (0.3538, 0.3538, 0.3742). The 12 times greater multiplicity of the latter position requires a fractional occupation, which was established to be around 7.5%, indicating ~90% filling fraction of the cage. Similar off-centering has already been described for $Na_{22}Si_{136}$,[6] in which the Na atoms in the ($5^{12}6^4$) cages are moved to site 32*e*, and the filling fraction is below 80%. The framework building Sn and Ga atoms in compound **2** share all three sites 96*g* (Sn:Ga = 68:32), 32*e* (Sn:Ga = 91:9), and 8*a* (Sn:Ga = 62:38), respectively, in a manner very similar to the distributions in compound **1**. Therefore, $[Rb^+]_7[(Rb^+)_{0.17}(Ba^{2+})_{0.83}]_{16}[4b\text{-}Ga^{1-}]_{36}[4b\text{-}Sn^0]_{100}$ also accounts for a Zintl phase.

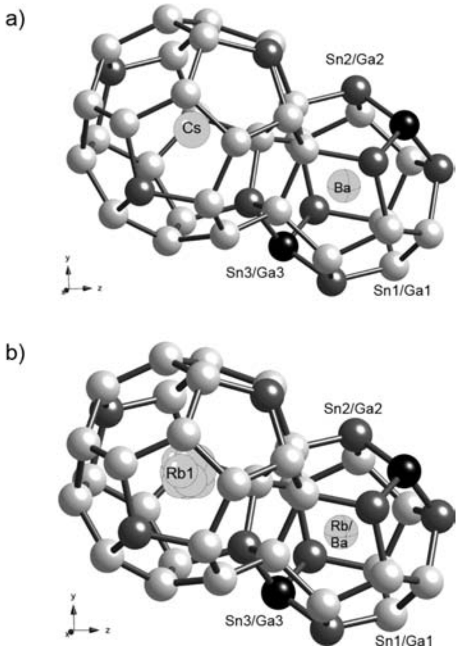

Figure 2. Pentagonal dodecahedra and hexakaidecahedra with the corresponding guest atoms *a*) Cs (on site 8*b*) and Ba (on 16*c*) in **1** and *b*) of Rb1 (on split site 96*g*) and Ba/Rb (on 16*c*) in **2**. In **3** and **4**, the larger $(Sn/Ga)_{28}$ cages are empty.

Last, we focus our attention on compound **4**, where the Ba atoms are located only in the pentagonal dodecahedra. Its composition is the same as the previously known clathrate $Ba_{16}Ga_{32}Sn_{104}$,[12] however, the cell parameters in both cases are clearly not identical (a = 16.9963(15) vs a = 17.054(1) Å).[18] The mixed occupied framework sites are also refined differently; Sn:Ga ratios of 74:26 (96*g*), 85:15 (32*e*), and 71:29 (8*a*) from the literature[12] vs 70:30 on 96*g*, 59:41 on 8*a* and a full occupancy with Sn atoms on 32*e* in our compound **4**. Since in our studies we followed the exact same experimental procedure as outlined in the earlier publication, the only logical supposition is that an inclusion of K in $Ba_{16}Ga_{32}Sn_{104}$ had occurred after all,[12] although the small K content had not been verified. In our case too, the type II compound could not be obtained by reactions without Na as a starting material, but neither the refinements nor the elemental analysis on **4** could confirm the presence of elements other than Ba, Ga, and Sn in the structure. Therefore, we might reason that our refined structure is closer to the idealized $Ba_{16}Ga_{32}Sn_{104}$ phase with the type II structure.

All of the above brings us to the concluding part of this communication, which sums up two of the most prominent aspects of the crystal chemistry of the new compounds. First, the above-mentioned "anomalies" in the unit cell volumes of $Cs_8Ba_{16}Ga_{40}Sn_{96}$, from the structure description, it is apparent that two distinct scenarios must be considered. In structures **3** and **4**, only the small $(Sn/Ga)_{20}$ cages host guest atoms, while in structures **1** and **2**, the larger $(Sn/Ga)_{28}$ cages are also (nearly) filled. Based on this alone, an expansion of the unit cells on going from Na to Cs is to be expected. However, as more alkali metals are accommodated in the cages of the structure, the Ga content increases progressively and is maximized at 40 of the 136 framework atoms for $Cs_8Ba_{16}Ga_{40}Sn_{96}$. Notice that Ga is smaller than Sn, hence, the lattice is expected to contract. In the case of the Rb compound, because of the incomplete filling of the larger cavities and the small admixture of Rb and Ba in the pentagonal dodecahedra, there are 4 fewer Ga atoms substituting Sn at the framework atoms, which is the reason why the cell parameter in **2** (a = 17.0367(5) Å) is bigger than that of **1** (a = 17.0283(5) Å). In structures **3** (a = 17.0292(6) Å) and **4** (a = 16.9963(15) Å), the "matrix" effect of the filler atoms is diminished due to one-third of the cages being empty, but the mixing of the larger K atoms with Ba on site 16*c* (and the concomitant decrease of the Ga content) accounts for the observed trends.

Second, guest atoms in clathrates are often described as "rattlers",[2,15b,19] therefore, we specifically note the thermal parameters of the Rb and Cs atoms in the large ($5^{12}6^4$) cage. As discussed already, the Cs atoms have nearly the perfect size to fill the hexakaidecahedra, while the Rb atoms are smaller and also fit, but loosely. Hence, the Rb atoms would be better "rattlers", as also evidenced by their off-centering to site 96*g* (Figure 2). Temperature-dependent X-ray diffraction work between 100 and 250 K shows that the guest atoms in the cages "vibrate". Such behavior in clathrate compounds can be described as an Einstein oscillator in a Debye host solid (= framework atoms).[2,19] The ADP data can be used to estimate the Einstein temperature Θ_E of the rattlers and the Debye temperature Θ_D of the host framework and to calculate with the resulting values the heat capacity C_v and velocity of sound v_s of each compound.[20] Thereby, the lattice thermal conductivity (at 200 K) can be determined with $\kappa_{lat} = 1/3C_v v_s d$ (d is mean free-path of the phonons)[20] to $\kappa_{lat} \approx 0.0054$ W/cm·K for **1**, 0.0052 W/cm·K for **2**, 0.0050 W/cm·K for **3**, and 0.0047 W/cm·K for **4**. Low κ_{lat} values like these estimations are an important prerequisite for improving the thermoelectric figure-of-merit zT[2,19] and may suggest that, via optimizations/fine-tuning the structures of the presented type II clathrates, one might find compounds with characteristics of the coveted "phonon-glass electron-crystal" (PGEC) material, as coined by Slack.[2]

ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic information, synthesis details, and structural characterization, EDX analysis, additional structural discussion. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support from the University of Delaware and U.S. Department of Energy through grants DE-SC0001360 and DE-SC0008885. We also thank Mrs. Hua He and Mr. Liu Chang for the EDX measurements.

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(14) The 5^{12} and $5^{12}6^4$ nomenclature, after ref 3, denotes the 20-atom polyhedra with 12 pentagonal faces and the 28-atom polyhedra with 12 pentagonal and 4 hexagonal faces, respectively.

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(17) To illustrate the preferential filling of the cages, we use the ionic radii according to Shannon and Prewitt (Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr.* **1969**, *B 29*, 925):$r \approx 2.02$ Å for Cs^+, 1.86 Å for Rb^+, 1.78 Å for K^+, and 1.53 Å for Na^+. Ba^{2+} with an ionic radius of $r \approx$ 1.75 Å has nearly the same size as K^+ cation.

(18) Caution needs to be exercised here because the data collections are not at the same temperature. The cell parameter a = 17.054(1) Å at room temperature from ref 12 is very close to the extrapolated value of 17.045 Å for the K-containing representative **3**.

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