Clathrate III of Group 14 Exists After All

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The interest in clathrate frameworks made of elements of group 14 has not only reemerged recently, 35 years after their discovery, but has skyrocketed because of their theoretical potential for high thermoelectric efficiency. Prior to this work, only two of the clathrate prototypes initially identified for the hydrate inclusion compounds, those of types I and II, were known for compounds of group 14 elements. Of these two types, until very recently, only clathrate I (ideal formula A$_8$Tt$_{46}$ where A = alkali metal, Tt = Tetrel is Si, Ge, Sn) was relatively well studied, while clathrate II (ideal formula A$_2$Tt$_{136}$) was somewhat ignored because of inability to synthesize it as a pure phase with defined compositions, and in a rational and reproducible way. This problem was overcome by realizing that the voids in clathrate II differ significantly in size from each other, and therefore two very different alkali metal cations such as Na and Cs or Na and Rb are needed to “stabilize” the structure. This approach lead to the rational synthesis of the pure and stoichiometric clathrate II compounds (Cs or Rb)$_3$Na$_{10}$Tt$_{172}$-3. Nevertheless, in addition to types I and II, there are other clathrate types that are known for the hydrate inclusion compounds but that are only theoretically considered and debated for the elements of group 14.4

We have now made the first clathrate III of an element of group 14. Synthesized and structurally characterized are Cs$_3$Na$_{13.33}$-10-Sn$_{172-3}$ and Cs$_{13.8(1)}$Rb$_{16.2(1)}$Na$_{10}$Sn$_{172-3}$ where $x \approx 9.6(2)$ with this structure. The two new compounds of ideal formula of A$_3$Sn$_{172}$ are isosstructural with inclusion compounds of the clathrate III type such as [Br$_2$$_2$]$[\text{H}_2\text{O}]$; and [CH$_2$CH$_2$OH]$_3$ClO$_4$. (1) for example, where $\square$ denotes a vacancy. Initially Cs$_3$Sn$_{13.33}$-10-Sn$_{172}$ was identified as a byproduct from a reaction designed to explore the stoichiometry range of another clathrate-related compound, Cs$_3$Na$_{10}$Sn$_{23}$, the structure of which is made of layers of clathrate II that are intercalated with sodium cations and tin tetrahedra.5 Later, after the structure and compositions were determined from single-crystal X-ray diffraction studies, the compound was synthesized in high yields from more appropriate stoichiometric mixtures.6 Nonetheless, traces of Cs$_3$Sn$_{14}$ with the clathrate I structure were found in the products. This is not surprising since the ratios of Cs to Sn in the two compounds, 1:5.50 and 1:5.43 for clathrates I and III, respectively, are virtually identical, and the only difference is the small amount of sodium available for clathrate III. Thus, small excess of sodium leads to much better yields but with traces of other phases such as Cs$_3$Sn$_{13.33}$-10Sn$_{172}$, (isostructural with Cs$_3$Sn$_{17}$)$_8$Na$_{23}$, and Cs$_3$Na$_{10}$Sn$_{23}$.6 To avoid these we also used excess of tin which resulted in “harmless” elemental tin in the product. The clathrate III compounds are very brittle, dark-gray to black in appearance, diamagnetic, and air- and moisture-stable.10

The structure of the new clathrate phases was determined from three single crystals selected from reactions loaded with different compositions.11 The reason was to ascertain the exact formula of the clathrate and to determine whether the ratio of alkali metal to tin can vary. Like the structures of clathrates I and II, the structure of clathrate III is a three-dimensional cage-like framework of four bonded tin atoms (Figure 1). There are three different cages in this clathrate: of 20 atoms and 12 pentagonal faces (5/2), of 24 atoms and 12 pentagonal and 2 hexagonal faces (5/2), and of 26 atoms and 12 pentagonal and 3 hexagonal faces (5/6). These cages are in a ratio of 10:6:4, respectively, or a total of 30 per unit cell, and are all condensed by face-sharing. The available 30 large alkali-metal cations of sodium, rubidium and cesium fill all of the cages. The ideal tin framework, that is, without vacancies, is built of 172 atoms per cell distributed over 17 crystallographic sites and has lower density than clathrates I and II.5 The ideal formula of the compound, therefore, would be A$_3$Sn$_{172}$. However, there are certain defects in the framework, predominantly pairs of missing tin atoms, which seem to be a necessary condition for the formation of this clathrate structure. Furthermore, these defects lead to a composition that corresponds to an electronically balanced, diamagnetic compound, a Zintl phase. All atoms in an ideal, defect-free framework of a clathrate of any type are four-bonded and therefore neutral. Thus, the electrons brought by the alkali metals are “extra” and would populate the conduction band of the framework and make the compounds metallic. This is observed for clathrate II (Rb or Cs)$_3$Na$_{10}$(Si or Ge)$_{136}$, where the framework is without defects, and the 24 cations bring that many extra electrons and the compounds are metallic. Some of the clathrate I compounds such as (K or Rb)$_3$(Ge or Sn)$_6$Cl$_2$, on the other hand, have two vacancies per formula.12 Each of these vacancies generates four three-

(5) X-ray diffraction data were collected with graphite-monochromated Cu Kα radiation on three crystals from three different reactions. The structures were solved by direct methods in P4/mmm and were refined on F using the SHELXL-97 package, Crystallographic Information File. A full sphere of data (2$\theta_{max}$ = 56°) was collected on a Bruker APEX CCD diffractometer at 153(2) K and corrected for absorption with SADABS. The crystal (0.10 x 0.08 x 0.06 mm) was selected from a reaction loaded as Cs$_3$Na$_{10}$Sn$_{23}$. Crystal data: a = 23.5389(9) Å and c = 12.1031(7) Å, Z = 1, $\mu$ = 188.43 cm$^{-1}$, $d_{calc}$ = 5.782 g cm$^{-3}$, R1/wR2 = 5.46/9.99% for 4213 observed (I > 2$\sigma$(I)) reflections and 151 variables. Cs$_3$Na$_{10}$Sn$_{23}$ is an octant of a sphere of data (2$\theta_{max}$ = 70°), rather than the conventional limit of 2$\theta_{max}$ = 50°) was collected on a CAD4 single-crystal diffractometer at 293(2) K and the data were corrected for absorption with the average of 5$\gamma$-scans. The crystal (0.12 x 0.10 x 0.08 mm) was selected from a reaction loaded as Cs$_3$Na$_{10}$Sn$_{23}$. Crystal data: a = 23.5566(9) Å and c = 12.1040(9) Å, Z = 1, $\mu$ = 187.8 cm$^{-1}$, $d_{calc}$ = 5.765 g cm$^{-3}$, R1/wR2 = 8.24/15.34% for 6289 observed reflections (I $\geq$ 2$\sigma$(I)) and 151 variables. Cs$_{12}$Sn$_{17}$(Si or Ge)$_{17}$ is an octant of a sphere of data (2$\theta_{max}$ = 70°), rather than the conventional limit of 2$\theta_{max}$ = 50° was collected on a CAD4 single-crystal diffractometer at 293(2) K and the data were corrected for absorption with the average of 5$\gamma$-scans. The crystal (0.10 x 0.10 x 0.06 mm) was selected from a reaction loaded as Rb$_3$Cs$_3$Na$_{10}$Sn$_{23}$. Crystal data: a = 23.4901(1) Å and c = 12.087(1) Å, Z = 1, $\mu$ = 196.87 cm$^{-1}$, $d_{calc}$ = 5.617 g cm$^{-3}$, R1/wR2 = 4.25/8.61% for 2087 observed reflections (I $\geq$ 2$\sigma$(I)) and 152 variables.
Sn 162.3(1), and (Cs 13.8 Rb 16.2)Na 2.8 Sn 162.4(1), that is, Na (1.33 x 10^10)Sn (172 x 10^10) that yielded the following formulas: Cs 30 Na 2.5 Sn 162.6(1), Cs 30 Na 2.9.

The sodium distances to the six neighboring tin atoms (broken open bonds in a negative charge of 6. The sodium distances to the six neighboring tin atoms (broken open bonds in b) are normal for Na–Sn.

The eight alkali metal atoms per formula counterbalance these negative charges, and the compounds are diamagnetic and electronically balanced.

Missing in clathrate III are predominantly pairs of neighboring tin atoms, all edges of the 26-atom cages. Furthermore, for every missing pair of framework atoms a single sodium cation takes the position that is half-way between the two vacancies (Figure 2). There are two such places in the structure. One is a pair of equivalent atoms that are at an impossibly short distance of 2.39 Å from each other if both are present at the same time. The corresponding position refines as occupied only 25%, and since there are four such pairs in the unit cell, it means that on average two of them are completely missing and only one position of the other two is occupied. Two sodium atoms are refined at the places of the two missing pairs. The second place of missing pairs in the structure is a little more complicated to explain. There are eight equivalent pairs made of a four-fold position that is occupied about 50% and an eight-fold position that is occupied about 80%, and the distance between these two positions is rather “normal”, 2.73 Å. Again, a sodium atom is found at the center of the pair when the latter is missing. It should be pointed out that a missing pair of atoms generates six negative charges, that is, two fewer than the eight negative charges that would be generated by two separate vacancies. These considerations along with the requirement for electronically balanced compound from the measured diamagnetism provide the formula of the compound as A30 Na11.33–x Sn13–2x.

The three independent structure refinements yielded the following formulas: C83Na82Sn162.6(1), C83Na82.9Sn162.3(1) and (C313Rb6.2Na2.9Sn62.6(1)), that is, x in the general formula is nearly identical for the three compounds. This suggests that clathrate III is a “line compound”, that is, a compound with a very narrow stoichiometry range and, for simplicity, can be formulated as C83Na82Sn162. As expected the Sn–Sn distances of the atoms neighboring the vacant sites are shorter than the rest of the distances in the framework. Also, the openings created by the missing pairs are of very suitable sizes for the sodium atoms (Figure 2) since the distances to the neighboring tin atoms, 3.30–3.40 Å, are quite typical for Na–Sn. It should be mentioned here that quite often the clathrate III structure of the hydrates is similarly stabilized by tetraalkylammonium salts such as fluorides or benzoates, where the fluorine or the oxygen of the benzoate replaces water molecules of the framework while the cation R3N+ occupies the cages.

It is relevant to discuss the rationale in forming preferably clathrate III rather than clathrates I and II for these particular compositions. The stabilization of a clathrate framework is a subject of a delicate balance between the sizes of the guest and host atoms, where the latter defines the radius of a cage made of a particular number of atoms. Guests, that is, cations in our case, of equal or similar sizes would favor the formation of a clathrate structure with cages made of similar number of atoms. This is the case of clathrate I which is built of 20- and 24-atom cages, and therefore can be and is stabilized by one type cations of suitable size. Thus, the clathrate I framework made of silicon can be stabilized with Na or K but not with Rb or Cs. Analogously, clathrate I made of germanium forms only with K, while the same clathrate structure of tin forms predominantly with Rb or Cs. Clathrates with very different cages, on the other hand, are stabilized by two or more types of cations of very different but appropriate for the cages radii. Such is the case of the clathrate II compounds (Rb or Cs)8Na16(Si or Ge)136 where the available 28- and 20-atom cages are filled with Cs and Na or Rb and Na, respectively. However, this structure cannot be made of tin simply because even the largest available cations, those of cesium, are not big enough to fit in the 28 atom cages made of the larger tin. In other words, the choice and availability of “templates” control the type of clathrate framework to be formed. Yet a way to circumvent the lack of large enough cations is to increase their numbers, that is, to further reduce the system and, therefore, to break bonds and create more space that can be stuffed with cations. This is exemplified in the structure of C83Na82Sn123 where clathrate layers made by “cutting” some of the bonds of the 28-atom cages of clathrate II are intercalated with sodium cations and additional Sn4 tetrahedra. Clathrate III is stabilized similarly since for each missing pair of tin atoms broken are six bonds, and the “recovered” space is occupied by a cation. The three different cages of this clathrate can potentially accommodate different cations as well, and combinations such as K6Si30, K6Rb6Si30, Rb10Cs20- and, of course, the observed Cs30 can be suggested. The product of the reaction with mixed Rb and Cs (and Na), the compound C83Na13Rb62Na2Si28,11 clearly showed Cs and Rb preferentially occupying the 26- and 20-atom cages, respectively, while the medium-sized 24-atom cages were occupied by a statistical mixture of Rb and Cs refined as 52 and 48%, respectively.

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Supporting Information Available: An X-ray crystallographic file for the three structure refinements, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Assuming the presence of a sodium atom (N) and (N) are the numbers of sodium atoms at the two pairs of defects described in the text) every time a pair of tin atoms is missing (V1 is the number of vacancies of the eight pairs of symmetry-related atoms, and V1 and V4 are the numbers of vacancies of the four-fold and eight-fold atoms, respectively, that form the second set of eight pairs described in the text) we can derive the following negative charges due to the vacancies: (6N1 + 6N2) is the charge due to missing pairs, and (V1 − 2N1) x 4, (V1 − N1) x 4, and (V4 − N4) x 4 are the charges due to missing single atoms of the three types. The sum of these must equal the number of available cations which is 30 cesium and (N1 + N2) sodium atoms, i.e., (6N1 + 6N2 + (V1 − 2N1) x 4 + (V1 − N1) x 4 + (V1 − N1) x 4 + 30 + N1 + N2). This can be simplified into 3(N1 + N2) = 4(V1 + V4 + V3) − 30, and when the sum of the vacancies is labeled the number of sodium atoms in the formula becomes 4/3 x 70 and the overall formula is C83Na82.33–x Sn13–2x.