DOI: 10.1002/anie.200806158

Clathrates

The Antimony-Based Type I Clathrate Compounds $Cs_8Cd_{18}Sb_{28}$ and $Cs_8Zn_{18}Sb_{28}$**

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Dedicated to Professor Xin-Tao Wu on the occasion of his 70th birthday

The term clathrate pertains to a large family of inclusion compounds that feature a complete isolation of guest atoms by a host framework.[1] Recently, type I clathrates have attracted considerable interest among experimental and theoretical chemists:[2] not only is the nature of their bonding remarkably diverse, but such phases may also exhibit interesting and potentially useful physical properties, particularly superconductivity[3,4] and thermoelectricity.[5,6] The earliest studies concerned the nominal cubic A_8Tt_{46} members (A = alkali or alkaline earth metal, Tt = Si, Ge, Sn). These structures raised particular bonding problems, namely that the characteristic framework of fourfold-bonded Tt atoms should be electron-sufficient (closed-shell) without any need for reduction by A atoms.[7a] This contradiction was resolved in two ways: 1) evidence that specific Tt vacancies on that sublattice in fact afford valence-precise 184-electron A_8Tt_{44} compositions,[7b] such as $Rb_8Sn_{44}\square_2$[2a,7c] and $Cs_8Sn_{44}\square_2$ (□: vacancy) in a 2 × 2 × 2 superstructure ($Ia\bar{3}d$),[7d] and 2) appropriate substitutions of electron-poorer elements for Tt yield vacancy-free products, such as $Ba_8In_{16}Ge_{30}$, $Ba_8Cd_8Ge_{38}$,[2m] $Cs_8Zn_4Sn_{42}$,[2e] and $A_8Hg_4Sn_{42}$ (A = K, Rb, Cs).[2n] Such phases thus afford a wide range of essentially valence (closed-shell) and nominally semiconducting compounds, although these conditions may not always apply on substitution of earlier main-group elements.[8]

Very few type I clathrates with framework elements other than Group 14 have been described. For example, elements of Group 15 or higher have been reported in clathrate I examples only as compensated dopants in Group 14-based networks or on cation sites in inverse examples, such as $Ba_{8.00}Ga_{17.31}Ge_{25.90}Sb_{2.15}$, $Ge_{38}Sb_8I_8$, $Sn_{38}Sb_8I_8$, and $Ge_{30}P_{16}Te_8$.[9] Furthermore, the only reported phosphorus example, $Ba_8Cu_{16}P_{30}$, exists in an orthorhombic superstructure (*Pbcn*) of the type I clathrate, although no studies of its possible composition range or electronic balance have appeared.[10] On the other hand, introduction of heavier Group 15 elements into the clathrate I members seems very feasible, and could facilitate improved thermoelectric properties.

Herein we report reproducible syntheses of the first stoichiometric, classical antimony-based clathrate I phases for $Cs_8Cd_{18}Sb_{28}$ and $Cs_8Zn_{18}Sb_{28}$ by reactions of the elements at 550 °C. The structures (see the Expermimental section; $Pm\bar{3}n$, No. 223) are depicted in Figure 1. As in other structures of this type, three distinctive crystallographic sites define the framework: 6*c* (Cd1 or Zn1/Sb1), 16*i* (Sb1 or Zn2/Sb2), and separate 24*k* (Cd2/Sb2 or Zn3/Sb3). These sites produce the characteristic non-intersecting chains of 24-atom tetrakaidecahedra that share both opposed hexagonal faces and side faces with intervening 20-atom pentagonal dodecahedra. The two polyhedra occur in 6:2 proportions, and are generated entirely by fourfold-bonded Zn/Cd and Sb atoms. The guest cesium atoms on 6*d* and 2*a* sites fully occupy the centers of all 24- and 20-atom clusters, respectively. Note that the isotropic

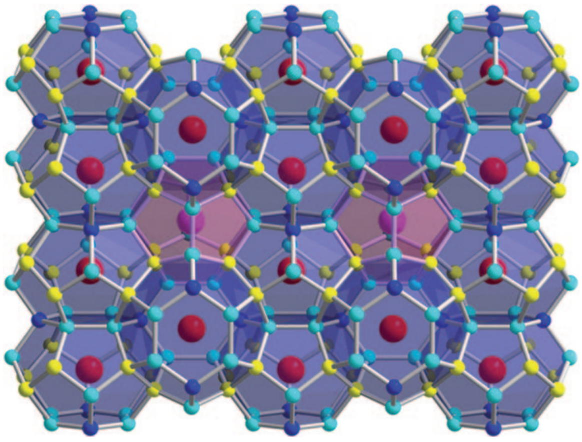

Figure 1. The structure of type-I clathrates $Cs_8Cd_{18}Sb_{28}$ or $Cs_8Zn_{18}Sb_{28}$ projected approximately along the *a* axis. Cyan: 24*k* Cd2/Sb2 or Zn3/Sb3; blue: 6*c* Cd1 or Zn1/Sb1; yellow: 16*i* Sb1 or Zn2/Sb2; magenta: 2*a* Cs1; red: 6*d* Cs2. Pentagonal dodecahedra are shown in lavender, and the tetrakaidecahedra in dark blue.

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[**] This work was supported by the National Natural Science Foundation of China under Projects (20773130, 20733003, 20821061), "Key Project from Fujian Institute of Research on the Structure of Matter" (SZD08002), and the "Key Project from Chinese Academy of Sciences" (KJCX2-YW-H01, CXJJ-219), 973 Program (2007CB815306, 2009CB939801). The work in the Ames Laboratory was supported by the Office of the Basic Energy Sciences, Materials Sciences Division, U.S. Department of Energy (DOE). We thank Mei-Chun Chen and Wu-Zui Zheng, and Hua Lin and Peng Wang for their help in confirmative experiments.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200806158.

atomic displacement parameter (ADP) of the Cs2 atom in the larger cavity (6*d*) is characteristically about 2.2–2.5 times that of Cs1 in the smaller site (2*a*),[11] and presumably reflects the "rattling" of Cs2 in the larger cluster.[2e] This displacement is also more pronounced in the larger cadmium cage.

In the $Cs_8Cd_{18}Sb_{28}$ structure, the sites 16*i* and 6*c* are fully occupied by Sb1 and Cd1 atoms, respectively, whereas the 24*k* site refines as 49.7(4) % Cd2, 50.3(4) % Sb2 (in effect 50:50), assuming full occupancy. Such a distribution is in good agreement with the concept of topological charge stabilization[12] and Mulliken population analyses;[13] that is, the framework site with the greatest Mulliken population is occupied by more electronegative species, and that with the lowest Mulliken population by more electropositive unit. Previous theoretical studies on K_8Si_{44} suggested that the 6*c* site has the lowest Mulliken population among the three in its clathrate I structure.[12] Therefore, an organization of atoms on framework sites according to Mulliken electronegativities (χ)[14] is indicated. The less electronegative cadmium atoms $(\chi_{Cd} = 4.33)$ prefer the 6*c* site, and the more electronegative antimony atoms (4.85) the 16*i* position; the 24*k* site is intermediate, and in this case mixed. These same differentiations are found for 6*c* vacancies in other A_8Tt_{44} phases, and among many ternary derivatives of Group 14 lattices that have substitutions with elements such as gallium, zinc, and copper to reduce the total electron counts in the networks to an optimal level (see above). The other new product, $Cs_8Zn_{18}Sb_{28}$, with a more intermediate electronegativity value for zinc of 4.45 has mixed zinc and antimony atoms in all three of the 6*c*, 16*i*, and 24*k* sites: 43.3(4) % Zn1, 56.7(4) % Sb1; 19.8(3) % Zn2, 80.2(3) % Sb2; and 50.4(3) % Zn3, 49.6(3) % Sb3, respectively. Zinc again dominates in the 6*c* and 24*k* sites. The larger degree of Zn/Sb disorder on the three framework sites parallels the Ga/Sn disorder in $Ba_8Ga_{16}Sn_{30}$.[2j] Interestingly, phosphorus also favors the 16*i* site in the inverse clathrate $Ge_{38}P_8I_8$.[9f] In contrast, antimony-doped $Ba_8Ga_{16}Ge_{30}$ clathrates, in which antimony is only 4.7 % of the framework, has a mixed Ge/Ga distribution in the inverse order (24*k* > 16*i* by about 2:1), but this is a more complex situation, at least because of size.[9a]

We allowed free refinements of occupancies for the unique host atoms during the structural analysis, but found no evidence for any vacancies. This case is different from $Rb_8Sn_{44}\square_2$, a defect type I clathrate with vacancies at the 6*c* site.[7c] The Cd–Sb and Cd–Cd bond lengths in $Cs_8Cd_{18}Sb_{28}$ range from 2.8046(8) to 2.863(2) Å, and the Sb–Sb distances from 2.825(2) to 2.8451(6) Å. In $Cs_8Zn_{18}Sb_{28}$, the Zn–Sb, Zn–Zn, and Sb–Sb distances all fall in the range of 2.6836(7) to 2.7363(5) Å. The Sb–Sb bond is about 4 % shorter than that in the former case because the involvement of smaller zinc generates a smaller framework. These metal–metal bond lengths are comparable to those found in related intermetallic compounds, such as Cd_6Sb_5,[15a] $Cd_{12.7(1)}Sb_{10}$,[15b] Cd_4Sb_3,[15c] α-Zn_4Sb_3,[15d] β-Zn_4Sb_3,[15e] $Zn_{6-\delta}Sb_5$,[15f] and $Zn_{13}Sb_{10}$.[15g] Some of the Cd/Sb and Zn/Sb binary compounds have shown promising thermoelectric properties.[15c,e,f]

It is noteworthy that the compositions obtained from the single-crystal refinements of $Cs_8Cd_{17.9(1)}Sb_{28.1(1)}$ and $Cs_8Zn_{17.9(2)}Sb_{28.1(2)}$ are indistinguishable from those for a typical Zintl phase,[13] $Cs_8M_{18}Sb_{28}$ (M = Cd, Zn), for which the formal oxidation states could be assigned as $(Cs^+)_8$-$(M^{2-})_{18}(Sb^+)_{28}$. The refinements are also in agreement with the energy-dispersive X-ray spectroscopy (EDX) results for $Cs_8Cd_{18.5(6)}Sb_{27.4(9)}$ and $Cs_8Zn_{17.6(5)}Sb_{28.8(6)}$ (Supporting Information, Figure S1) considering their intrinsically larger standard deviations. To probe the site occupancies further, the compositions of hand-picked single crystals were quantitatively determined with the aid of an Ultima-2 inductively coupled plasma emission spectrometer (ICP-OES). These results are closer to the single-crystal refinements, with Cd/Sb and Zn/Sb molar ratios of 18.2(5):27.7(5) and 18.0(2):27.9(8), respectively, which are indistinguishable from the ideal 18:28 ratio. Syntheses starting with the refined stoichiometries gave single-phase products according to the powder patterns (> 95 % on the basis of estimated detection limits; Figure 2).

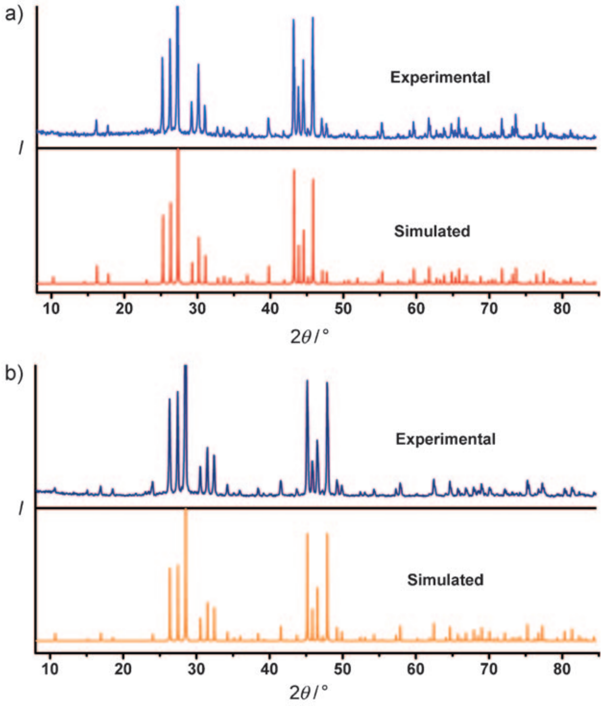

Figure 2. Experimental and simulated X-ray powder diffraction patterns of a) $Cs_8Cd_{18}Sb_{28}$ and b) $Cs_8Zn_{18}Sb_{28}$.

The possible phase breadth of $Cs_8Zn_{18-x}Sb_{28+x}$ was also explored starting with different loading ratios of Cs/Zn/Sb of $8{:}x{:}46-x$ (x = 12–20). Nonetheless, all reactions yielded the same major $Cs_8Zn_{18}Sb_{28}$ phase, and the diffraction data collected from tens of different single crystals from different reactions gave the same stoichiometry within the standard deviations. Similar experiments prove that the cadmium clathrate is also an evident line compound at this detection limit.

The densities of states (DOS) calculated by CASTEP,[16] some atomic projections thereof, and the electronic band structure for $Cs_8Cd_{18}Sb_{28}$ and $Cs_8Zn_{18}Sb_{28}$ are shown in Figure 3 and in the Supporting Information, Figure S2.

$Cs_8Cd_{18}Sb_{28}$ has a narrow band gap (ca. 0.06 eV), which is consistent with the Zintl concept mentioned above. As depicted in Figure 3 a, the bands below the Fermi level contain significant contributions from Cd 5s, 5p, and Sb 5s, 5p states, those above E_F being mostly Cd 5s, 5p and Sb 5p. On the other hand, bands between −7 and −13 eV are primarily Cs 5p and Cd 4d states. Strong hybridization between Cd 5p and Sb 5p states is indicated. Calculations show that $Cs_8Zn_{18}Sb_{28}$ has a similar electronic band structure (band gap circa 0.01 eV). The different substituent elements (Zn vs Cd) and the different disorder on the frameworks generate slightly different DOS around E_F, but the rather narrow gaps of these two compounds (Figure 3) reflect their semiconductor characteristics and their prospects as thermoelectric candidates. The corresponding thermoelectric property measurements are ongoing, and will be reported in a future full paper.

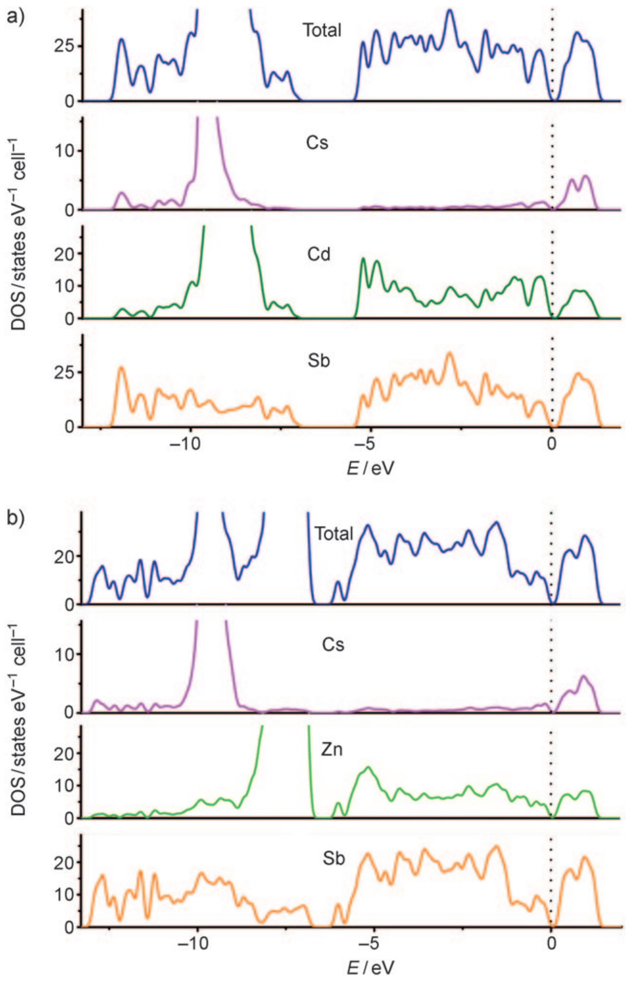

Figure 3. Total and partial density of states for a) $Cs_8Cd_{18}Sb_{28}$ and b) $Cs_8Zn_{18}Sb_{28}$.

The relatively small temperature-independent magnetic susceptibilities of $Cs_8Cd_{18}Sb_{28}$ (-4.5 to -5.1×10^{-4} emu mol^{-1}) and $Cs_8Zn_{18}Sb_{28}$ (-4.3 to -5.0×10^{-4} emu mol^{-1}) over 2–300 K (Supporting Information, Figure S3), indicate that they are both diamagnetic, which is in agreement with the electronic structure calculations.

In summary, the compounds $Cs_8Cd_{18}Sb_{28}$ and $Cs_8Zn_{18}Sb_{28}$ that were obtained by solid-state reactions lead to new directions for the chemistry of type I clathrate compounds. The two compounds have different disorder patterns in the framework, which appears to be related to the different electronegativities of cadmium, zinc, and antimony. These novel phases shed new light on chemical ranges among clathrate-type phases, and may lead to further superior thermoelectric materials. We expect to discover more new antimony, and perhaps arsenic, bismuth, and even tellurium clathrate compounds through tuning different combinations of elements in both the cages and the framework.

Experimental Section

All of the chemicals were purchased from Alfa Aesar China (UK, Tianjin) Co., Ltd. as chunks (Cs 99.98 %, Cd 99.95 %, Zn 99.99 %, Sb 99.99 %) and used without further purification in a glove box filled with dry N_2.

$Cs_8Cd_{18}Sb_{28}$ and $Cs_8Zn_{18}Sb_{28}$ are synthesized in high yields (> 95 % as determined by XRD patterns, with no extra lines observed) by reactions of the stoichiometric proportions of the elements in welded niobium containers that were sealed in an evacuated fused silica jacket (17 mm i.d.) under high vacuum (ca. 10^{-3} Pa). The assembly was heated at 550 °C for 10 days and then cooled at a rate of 5 °C h^{-1}. The gray powdery products contained block-shaped single crystals with a metallic luster. The $Cs_8Zn_{18}Sb_{28}$ crystals are silver-gray, and crystallize in pillar or block shapes with very good facets; $Cs_8Cd_{18}Sb_{28}$ favors block shapes. Both are stable in air at room temperature for at least half a month (checked by XRD), and both can be washed in water. Differential scanning calorimetry (DSC) diagrams of $Cs_8Zn_{18}Sb_{28}$ (Supporting Information, Figure S4) show an endothermic peak at 627 °C. X-ray powder diffraction analyses (Supporting Information, Figure S5) show that the compound is stable to 600 °C and then decompose into binary Zn–Sb phases, which is in good agreement with the results of the DSC analysis. The $Cs_8Cd_{18}Sb_{28}$ samples sealed in niobium tubing have been annealed at 550 and 600 °C, respectively, for 12 h and quenched in liquid nitrogen. The XRD analyses show that $Cs_8Cd_{18}Sb_{28}$ is stable at 550 °C and converts into a new orthorhombic $Cs_2Cd_5Sb_4$ phase at 600 °C ($Cmcm$, $a = 13.1704(9)$ Å, $b = 8.0153(7)$ Å, $c = 13.2434(11)$ Å, $V = 1398.04(19$ Å^3, to be published; see the Supporting Information, Figure S6). $Cs_8Cd_{18}Sb_{28}$ has also been synthesized in excess CsCl as a flux from mixtures with Lu, Cd, and Sb. The reaction mixture was loaded into a short fused silica tube (7 mm i.d., length 25 mm), in turn sealed in a larger evacuated fused silica tube container (10 mm i.d.), and then heated at 850 °C (i.e., well above the melting point of the CsCl solvent, 645 °C), for 4 days. The target crystals were obtained after washing the product with H_2O. Although no lutetium was found in the clathrate crystals as determined by the X-ray diffraction and the microprobe measurements, it serves as the crucial reducing agent in this pathway.

$Cs_8Cd_{18}Sb_{28}$: $M_r = 6496.04$, cubic, space group $Pm\bar{3}n$, $a = 12.1916(15)$ Å, $V = 1812.1(4)$ Å^3, $Z = 1$, $\rho = 5.953$ g cm^{-3}, $\mu = 19.344$ mm^{-1}, $F(000) = 2732$, $GOF = 1.381$, A total of 2448 reflections were collected and 403 were unique ($R_{int} = 0.0414$). $R1/wR2 = 0.0259/0.0446$ for 376 reflections ($I > 2\sigma(I)$) and 18 parameters.

$Cs_8Zn_{18}Sb_{28}$: $M_r = 5655.14$, cubic, space group $Pm\bar{3}n$, $a = 11.7054(16)$ Å, $V = 1603.8(4)$ Å^3, $Z = 1$, $\rho = 5.855$ g cm^{-3}, $\mu = 22.619$ mm^{-1}, $F(000) = 2410$, $GOF = 1.060$, A total of 11 429 reflections were collected and 360 were unique ($R_{int} = 0.0354$). $R1/wR2 = 0.0186/0.0381$ for 354 reflections ($I > 2\sigma(I)$) and 22 parameters.

The intensity data were collected on a Rigaku Mercury CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å) at room temperature. All absorption corrections were performed using multiscan. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with the SHELXTL-97 program package. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-420113 ($Cs_8Cd_{18}Sb_{28}$) and CSD-420114 ($Cs_8Zn_{18}Sb_{28}$).

Received: December 18, 2008
Revised: February 20, 2009

Keywords: antimony · clathrates · solid-state reactions · Zintl phases

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