J|A|C|S
COMMUNICATIONS

Assembly of Supertetrahedral T_5 Copper−Indium Sulfide Clusters into a Super-Supertetrahedron of Infinite Order

Le Wang,[†] Tao Wu,[†] Fan Zuo,[†] Xiang Zhao,[†] Xianhui Bu,[‡] Jianzhong Wu,[§] and Pingyun Feng*,[†]

Department of Chemistry, University of California, Riverside, California 92521, Department of Chemistry and Biochemistry, California State University, Long Beach, California 90840, and Department of Chemical and Environmental Engineering, University of California, Riverside, California 92521

Received November 28, 2009; E-mail: pingyun.feng@ucr.edu

Metal chalcogenide open frameworks built from tetrahedral clusters represent a unique family of materials that beautifully demonstrate the bottom-up self-assembly of nanoclusters with precisely defined size and composition. Such metal chalcogenide open frameworks preserve the structural features of condensed-phase semiconductors within a framework of three-dimensional (3D) porous architectures.[1−12] As such, they are capable of integrating uniform porosity with various physical properties such as semiconductivity, photoluminescence,[6b] photocatalytic activity,[6e] and thermoelectric behavior,[8a] making them potentially useful for different applications.

While different types of chalcogenide clusters are known,[2b,c,7b] the supertetrahedral T_n series of clusters (where n is the number of MX_4 tetrahedra along each tetrahedral edge) represent a unique family of tetrahedral clusters whose structures can be described as exact fragments of the well-known condensed phase of the cubic ZnS lattice. Since the report of $In_{10}S_{20}^{10-}$ T_3 supertetrahedral clusters in 1998,[3] the size of the synthetic supertetrahedral clusters has been increased to T_5 (e.g., $Cu_5In_{30}S_{56}^{17-}$ and $Zn_{13}In_{22}S_{56}^{20-}$) with 35 metal sites.[2c,6c] The size of such large T_n clusters is comparable to that of the smallest semiconductor quantum dots prepared from colloidal systems. However, the latter have less well-defined size and composition and do not form highly ordered crystalline lattices amenable to single-crystal X-ray diffraction (XRD) study. Furthermore, T_n clusters can be used as artificial tetrahedral atoms for the construction of crystalline molecular, supramolecular,[8b,11c] and covalent superlattices. As a result, the synthesis of large supertetrahedral clusters is highly desirable yet continues to be very challenging.

Supertetrahedral clusters without surface-capping organic ligands tend to form polymeric lattices. A common mode of linkage between adjacent supertetrahedral clusters uses a bicoordinate corner S^{2-} (or Se^{2-}) site as the cross-linker.[3c,4,6] In general, this type of linkage leads to various 3D open-framework architectures that are based on supertetrahedral cluster building blocks. However, in some rare cases, four T_n clusters have been found to form a closed polyhedral structure that in fact can be described as a supertetrahedron of supertetrahedra (also called a super-supertetrahedron), denoted as $T_{p,q}$, in which T_p clusters are further arranged into T_q clusters.[5] To date, only two types of $T_{p,q}$ clusters are known: $p =$ 2 or 4 and $q = 2$. In $T_{2,2}$ clusters [e.g., $M(III)_xM(IV)_{4-x}S_8^{x-}$, where M(III) = Ga, In and M(IV) = Ge, Sn], four T_2 clusters are arranged into a T_2 cluster,[6b] whereas in the $T_{4,2}$ cluster ($[Cd_{16}In_{64}S_{134}]^{44-}$), four T_4 clusters are assembled into a T_2 cluster.[5]

Here we report an extraordinary example in which an infinite number of the largest known Cu−In−S supertetrahedral clusters (T_5) are further assembled into a supertetrahedron of infinite order, denoted as $T_{5,\infty}$ (Figure 1 and Figures S1 and S2 in the Supporting Information). In other words, the whole crystal is a giant piece of a super-supertetrahedron whose order is limited only by the dimensions of the crystal.

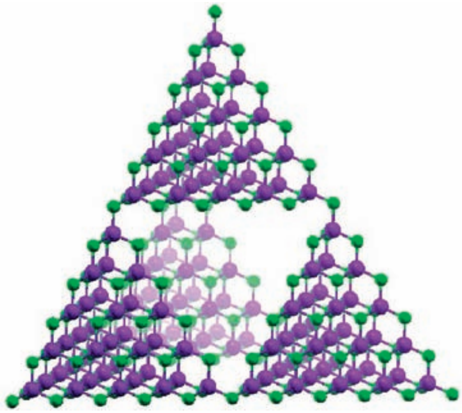

Figure 1. Four T_5 clusters, $M_{35}S_{53}$ (M = Cu^+, In^{3+}) organized into a secondary supertetrahedron with infinite order. Here, the super-supertetrahedral cluster is drawn as $T_{5,2}$ even though the actual structure is $T_{5,\infty}$. Color key: purple, metal; green, sulfur.

In this work, such an extraordinary super-supertetrahedron was experimentally realized in the Cu−In−S domain, and single-crystal XRD revealed a material (denoted as CIS-11) with a framework composition of $Cu_7In_{28}S_{53}^{15-}$ charge-balanced by fully disordered extraframework organic cations (protonated dibutylamine or isopropylcyclohexylamine).[13]

The most fascinating structural feature of CIS-11 is its dual hierarchical architecture. CIS-11 is one of the rare examples of an inorganic structure representing the expansion of the same packing mode on the atomic scale to a secondary hierarchy on the nanoscale, because other than the difference in dimension, the arrangement and orientation of the tetrahedral metal atoms within the T_5 cluster are exactly identical to the arrangement and orientation of the T_5 clusters in the whole crystal.

The formation of this $T_{5,\infty}$ cluster relies on a structural feature that had not been previously found in open-framework chalcogenides built from tetrahedral clusters. This unprecedented structural feature is the tetracoordinate corner sulfur atom (Figure 2). This tetracoordinate vertex is ideally tetrahedral and has an M−S−M angle of 109.5°. As a result, the corner tetrahedral S^{2-} sites and T_5 clusters (serving as pseudotetrahedral atoms) interconnect to create a 3D framework. In comparison, in previously reported chalco-

---

[†] Department of Chemistry, University of California, Riverside.
[‡] California State University, Long Beach.
[§] Department of Chemical and Environmental Engineering, University of California, Riverside.

10.1021/ja9100672

genide 3D frameworks, the supertetrahedral clusters are linked with bicoordinate corner S^{2-}/Se^{2-} sites into four-connected networks or, in only one case, with tricoordinate S^{2-} sites into the C_3N_4-type topology.[6d]

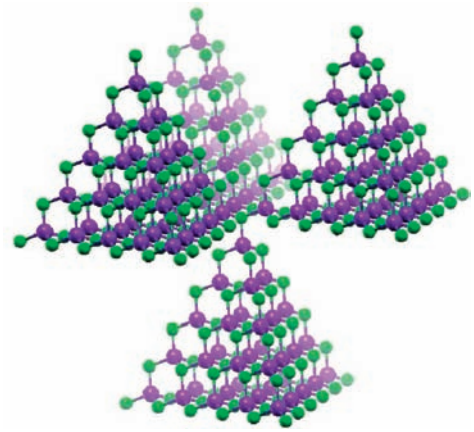

Figure 2. One tetracoordinate corner sulfur atom joining four T_5 clusters into a tetrahedral geometry, which is further extended into a 3D infinite framework in CIS-11. Color code: purple, metal; green, sulfur.

Following Pauling's electrostatic valence rule and consistent with previously reported structures, each corner sulfur atom and four core sulfur sites of T_5 clusters in CIS-11 are assigned an average of two Cu(I) and two In(III) sites to balance the local charge of the tetrahedral S^{2-} sites. The crystallographic refinement further supports such an assignment of the Cu(I) and In(III) ions around the tetrahedral sulfur. The short metal−sulfur bond length of 2.25 Å, compared with the typical In−S bond length of 2.4−2.5 Å, is another indication of the partial copper sites around the tetrahedral S^{2-} atom.

The above description of the CIS-11 structure highlights an exceptional bottom-up assembly approach for creating a hierarchical architecture ranging from the angstrom-length scale to the macroscopic millimeter scale. Equally impressive is that CIS-11 can be derived with an imaginary top-down approach by starting with a macroscopic piece of crystal with the cubic ZnS structure and periodically carving out the octahedral and half of the tetrahedral boxes of atoms (Figure 3). Thus, all of the atoms in this CIS-11 unit cell can be found at the exact positions of a 125-fold (5 × 5 × 5) ZnS zinc blende supercell with the rest of atoms being absent periodically. In other words, in such an imaginary top-down process, exactly 64.8% of the total of 1000 atoms in the 5 × 5 × 5 zinc blende supercell are etched out, with the 352 remaining atoms aligned as four supertetrahedral T_5 clusters. Consistent with such a removal of 64.8% of the atoms, a calculation using PLATON indicated that there is 60.2% extraframework void space, which is filled by fully disordered extraframework species.

Although the T_5 cluster building block itself already carries the fingerprint of the condensed phase (cubic ZnS in this case), the additional level of preservation in this "hollowed-out" bulk structure with all of the atomic sites preserved throughout the crystal is highly unusual. Such a precise atom-to-atom match between condensed and open-framework phases is another outstanding feature of CIS-11.

The synthesis of CIS-11 in the Cu−In−S domain was in part inspired by its similarity to the composition of copper indium sulfide ($CuInS_2$), which is one of the most studied semiconductor materials for high-efficiency solar cell applications. CIS-11 possesses a band gap of ~2.2 eV, as determined using solid-state UV−vis reflectance spectra with Kubelka−Munk methods (Figure S5), which indicates that the material retains the semiconducting property of the corresponding condensed phase. The relative blue shift of the optical band gap relative to condensed $CuInS_2$, which usually shows a band gap of 1.53 eV,[14] is also reasonable because the electrons are more localized as a result of the periodic absence of about two-thirds of the atoms and primarily confined within the nanosized T_5 building block. CIS-11 also shows photocatalytic activity for hydrogen evolution from water in the presence of Na_2S sacrificial reagent in the visible-light region (Figure S7).

CIS-11 with the $T_{5,\infty}$ structure (Figure 4) is currently the only synthesized member in a series of 3D porous frameworks that can be represented as $T_{n,\infty}$. The common condensed cubic ZnS-type structure can be represented as $T_{1,\infty}$. The synthesis of the $T_{5,\infty}$ structure reported here hints at the tantalizing possibility of synthesizing other members of the $T_{n,\infty}$ family. On the basis of Pauling's valence rule, the framework compositions of other members of the $T_{n,\infty}$ ($n = 2, 3, 4$) series of structures based on the Cu−In−S composition are listed in Table 1.

Table 1. Composition, Charge, and Percentage of Atoms Removed for $T_{n,\infty}$ Series of Structures Based on Cu(I)−In(III)−S Composition

structure	framework composition	charge per supertetrahedral cluster	percentage of atoms removed from the $n \times n \times n$ supercell
$T_{1,\infty}$	$(CuInS_2)_{1/2}$	0	0
$T_{2,\infty}$	$Cu_2In_2S_7$	−6	31.3
$T_{3,\infty}$	$Cu_2In_8S_{17}$	−8	50.0
$T_{4,\infty}$	$Cu_4In_{16}S_{32}$	−12	59.4
$T_{5,\infty}$	$Cu_7In_{28}S_{53}$	−15	68.4
$T_{n,\infty}$	$M_{(n)(n+1)(n+2)/6}S_{[(n+1)(n+2)(n+3)/6]-3}$		$1 - [(n+1)(n+2)(2n+3) - 18]/12n^3$

The "hollowed-out" bulk material provides an ideal platform for exploring how the material's properties may change upon

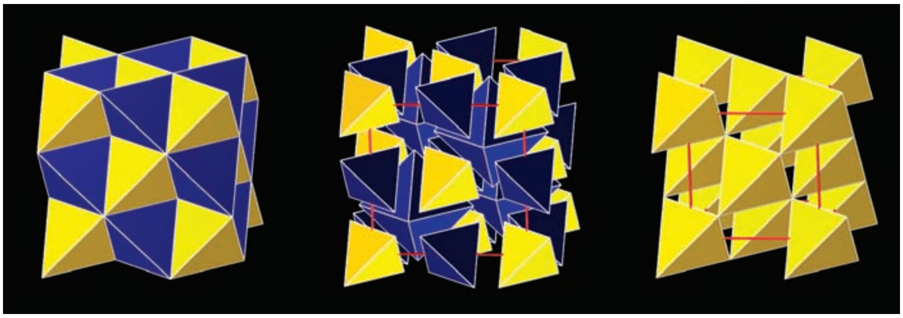

Figure 3. Illustration showing hollowed-out and remaining blocks in the condensed zinc blende-type phase. Yellow tetrahedra represent the remaining T_5 clusters, while blue tetrahedra and octahedra represent the hollowed-out space. (left) Actual representation of the structure, showing hollowed-out and remaining tetrahedra and octahedra. (middle) Separated blocks for better view. (right) Remaining blocks of atoms after removal of the carved-out blocks.

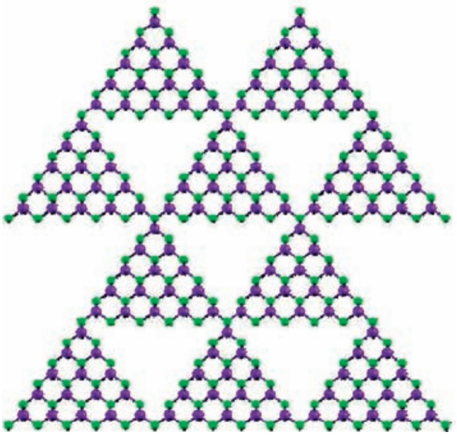

Figure 4. View of the 3D polymeric framework along the [110] direction of CIS-11.

periodic loss of inside atoms from a bulk single crystal. Theoretically, in addition to a decrease in particle size by chopping off outside atoms under the guidance of the quantum-confinement effect, another route for property engineering by periodically removing lattice atoms is also possible. Structures similar to CIS-11 but based on T_2, T_3, or T_4 clusters with comparable compositions (i.e., $T_{n,\infty}$ with $n = 2, 3, 4$; Table 1) would be promising candidates for tuning the properties of $CuInS_2$, and the work reported here suggests that the realization of such materials is feasible. This would serve to demonstrate a new principle of property engineering of semiconducting materials.

Acknowledgment. We are grateful for support of this work by the NSF (CHEM-0809335 and DMR-0907175 to P.F.), the Research Corporation (CC6593 to X.B.), and the DOE (DE-FG02-06ER46296 to J.W.).

Supporting Information Available: Synthetic procedures for CIS-11; dark-field optical images of crystals; experimental and simulated powder X-ray diffraction patterns; solid-state UV−vis absorption spectra; TGA plot; plot of visible-light-driven photocatalytic H_2 evolution; and crystallographic data, including positional parameters, thermal parameters, and bond distances and angles (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Krebs, B.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 769–788.
(2) (a) Scott, R. W. J.; MacLachlan, M. J.; Ozin, G. A. *Curr. Opin. Solid State Mater. Sci.* **1999**, *4*, 113–121. (b) Dance, I. G.; Fisher, K. G. *Prog. Inorg. Chem.* **1994**, *41*, 637–803. (c) Feng, P.; Bu, X.; Zheng, N. *Acc. Chem. Res.* **2005**, *38*, 293–303.
(3) (a) Parise, J. B.; Tan, K. *Chem. Commun.* **1996**, 1687–1688. (b) Cahill, C. L.; Parise, J. B. *Chem. Mater.* **1997**, *9*, 807–811. (c) Cahill, C. L.; Ko, Y.; Parise, J. B. *Chem. Mater.* **1998**, *10*, 19–21. (d) Cahill, C. L.; Parise, J. B. *J. Chem. Soc., Dalton Trans.* **2000**, 1475–1482.
(4) (a) Yaghi, O. M.; Sun, Z.; Richardson, D. A.; Groy, T. L. *J. Am. Chem. Soc.* **1994**, *116*, 807–808. (b) Li, H.; Laine, A.; O'Keeffe, M.; Yaghi, O. M. *Science* **1999**, *283*, 1145–1147. (c) Li, H.; Kim, J.; Li, H.; Eddaoudi, M.; Laine, A.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **1999**, *121*, 6096–6097. (d) Groy, T. L.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2001**, *123*, 4867–4868.
(5) Li, H.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2003**, *42*, 1819–1821.
(6) (a) Wang, C.; Li, Y.; Bu, X.; Zheng, N.; Zivkovic, O.; Yang, C. S.; Feng, P. *J. Am. Chem. Soc.* **2001**, *123*, 11506–11507. (b) Zheng, N.; Bu, X.; Wang, B.; Feng, P. *Science* **2002**, *298*, 2366–2369. (c) Bu, X.; Zheng, N.; Li, Y.; Feng, P. *J. Am. Chem. Soc.* **2002**, *124*, 12646–12647. (d) Bu, X.; Zheng, N.; Li, Y.; Feng, P. *J. Am. Chem. Soc.* **2003**, *125*, 6024–6025. (e) Zheng, N.; Bu, X.; Vu, H.; Feng, P. *Angew. Chem., Int. Ed.* **2005**, *44*, 5299–5303. (f) Zhang, Z.; Zhang, J.; Wu, T.; Bu, X.; Feng, P. *J. Am. Chem. Soc.* **2008**, *130*, 15238–15239. (g) Wu, T.; Wang, X.; Bu, X.; Zhao, X.; Wang, L.; Feng, P. *Angew. Chem., Int. Ed.* **2009**, *48*, 7204–7207.
(7) (a) Soloviev, V. N.; Eichhofer, A.; Fenske, D.; Banin, U. *J. Am. Chem. Soc.* **2001**, *123*, 2354–2364. (b) Corrigan, J. F.; Fuhr, O.; Fenske, D. *Adv. Mater.* **2009**, *21*, 1867–1871.
(8) (a) Mrotzek, A.; Kanatzidis, M. G. *Acc. Chem. Res.* **2003**, *36*, 111–119. (b) Palchik, O.; Iyer, R. G.; Liao, J. H.; Kanatzidis, M. G. *Inorg. Chem.* **2003**, *42*, 5052–5054. (c) Tsamourtzi, K.; Song, J.; Bakas, T.; Freeman, A. J.; Trikalitis, P. N.; Kanatzidis, M. G. *Inorg. Chem.* **2008**, *47*, 11920–11929.
(9) Bowes, C. L.; Huynh, W. U.; Kirkby, S. J.; Malek, A.; Ozin, G. A.; Petrov, S.; Twardowski, M.; Young, D. *Chem. Mater.* **1996**, *8*, 2147–2152.
(10) (a) Zimmermann, C.; Melullis, M.; Dehnen, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 4269–4271. (b) Dehnen, S.; Brandmayer, M. K. *J. Am. Chem. Soc.* **2003**, *125*, 6618–6619. (c) Dehnen, S.; Melullis, M. *Coord. Chem. Rev.* **2007**, *251*, 1259–1280. (d) Melullis, M.; Clerac, R.; Dehnen, S. *Chem. Commun.* **2005**, 6008–6010.
(11) (a) Vaqueiro, P.; Romero, M. L. *J. Phys. Chem. Solids* **2007**, *68*, 1239–1243. (b) Vaqueiro, P.; Romero, M. L. *Chem. Commun.* **2007**, 3282–3284. (c) Vaqueiro, P.; Romero, M. L. *J. Am. Chem. Soc.* **2008**, *130*, 9630–9631.
(12) Su, W.; Huang, X.; Li, J.; Fu, H. *J. Am. Chem. Soc.* **2002**, *124*, 12944–12945.
(13) Crystallographic data for CIS-11, $(Cu_7In_{28}S_{53})(C_8H_{18}NH_2)_{15}$: cubic, $F\bar{4}3m$, $a = 27.224(9)$ Å, $V = 20179(14)$ Å^3, $Z = 4$, Mo Kα, $T = 293$ K, $2\theta_{max} = 27.9°$, $R(F) = 9.80\%$ for 65 parameters and 375 reflections with $I > 2\sigma(I)$.
(14) Tell, B.; Shay, J. L.; Kasper, H. M. *Phys. Rev. B* **1971**, *4*, 2463.

JA9100672