

Pushing Up the Size Limit of Chalcogenide Supertetrahedral Clusters: Two- and Three-Dimensional Photoluminescent Open Frameworks from $(\text{Cu}_5\text{In}_{30}\text{S}_{54})^{13-}$ Clusters

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Received July 23, 2002

There has been an increasing interest in chalcogenide clusters during the past several decades.^{1,2} Very recently, the research on chalcogenide nanoclusters and nanoporous materials is evolving rapidly because of its relevance to nanoscience.^{3–8} In addition to the size-dependent property, chalcogenide nanoclusters also behave like artificial atoms and serve as building blocks for the construction of quantum dot superlattices.

For constructing open framework chalcogenides, we are particularly interested in clusters that are fragments of the zinc blende type lattice. One series of clusters that are exact fragments of the zinc blende type lattice are called supertetrahedral clusters denoted as T_n ($n = 2, 3, 4, \dots$).^{9–12} The formulas for discrete T_n ($n = 2–5$) clusters are M_4X_{10} , $M_{10}X_{20}$, $M_{20}X_{35}$, and $M_{35}X_{56}$, respectively, where M is a metal ion, and X is a chalcogen. When all corners of each cluster are shared through S^{2-} bridges, the number of anions per cluster in the overall stoichiometry is reduced by two.

We recently synthesized an open framework sulfide containing a cluster, $(\text{In}_{34}\text{S}_{54})^{6-}$, that resembles a regular T5 cluster, except that the core metal site is empty.¹³ It was realized that the formation of this pseudo-T5 cluster is related to the global charge matching between the inorganic framework and protonated amine molecules and the local charge matching surrounding core tetrahedral sulfur sites.^{10,11,13} On the basis of such an understanding, we focus on the heterometallic copper(I) indium sulfide with a goal to fill the empty core in the pseudo-T5 cluster. Another motivation to study copper indium chalcogenides is their useful semiconducting properties that make them efficient for use in areas such as photovoltaics.¹⁴ In this work, the partial substitution of indium by copper in the T5 cluster helps to generate a more negative framework. Locally, for clusters with tetrahedral sulfur sites, the coordination of sulfur to metal ions with different oxidation states such as Cu^+ and In^{3+} serves to maintain the local charge neutrality and prevent excessive positive charge around tetrahedral S^{2-} sites (Figure 1).

Here we report two open framework sulfides (denoted as UCR-16 and -17) that extend the maximum cluster size in known supertetrahedral clusters from 20 metal ions in a T4 cluster to 35 in a T5 cluster, $[\text{Cu}_5\text{In}_{30}\text{S}_{54}]^{13-}$. These T5 clusters are joined together to form a 2-D network in UCR-16 and a 3-D open framework in UCR-17 (Figures 2 and 3).¹⁵

To prepare UCR-16 and UCR-17, indium metal (398.6 mg), sulfur (276.0 mg), copper(I) sulfide (99.0 mg), and 4,4'-trimethylenedipiperidine (TMDP, 2.8325 g) were mixed with 50% ethylene glycol–water solution (5.0149 g) in a 23 mL Teflon-lined stainless steel autoclave and stirred for 30 min. The sealed vessel was then heated at 190 °C for 5 d. Mixtures of dark-orange platelike crystals

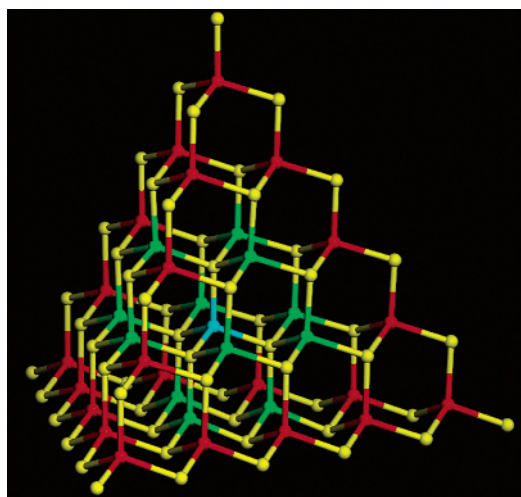


Figure 1. The structural diagram of a regular T5 cluster ($\text{Cu}_5\text{In}_{30}\text{S}_{54}$) showing 12 possible copper sites (in green) on four faces of the T5 cluster. Red, In^{3+} ; yellow, S^{2-} ; cyan, the core Cu^+ site. In a given cluster, only four green sites are occupied by Cu^+ ions. The occupation of green sites by Cu^+ ions is not random and follows Pauling's electrostatic valence rule.

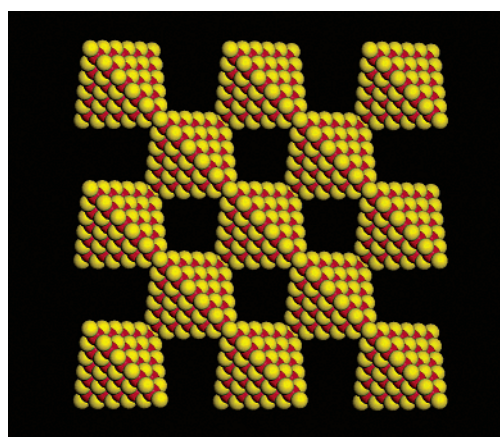


Figure 2. The top view of the two-dimensional sheet structure built from T5 supertetrahedral clusters in UCR-16.

(UCR-16, the major phase) and octahedral crystals (UCR-17) were obtained. Two phases can be manually separated. The pure phase of UCR-17 can be prepared when metal copper is employed as the starting material in place of copper(I) sulfide.

The most striking structural feature of UCR-16 and -17 is the presence of the T5 supertetrahedral cluster, $(\text{Cu}_5\text{In}_{30}\text{S}_{54})^{13-}$. The size of the T5 cluster as measured between corner metal sites is 1.6 nm, considerably larger than the T4 cluster that has a metal-

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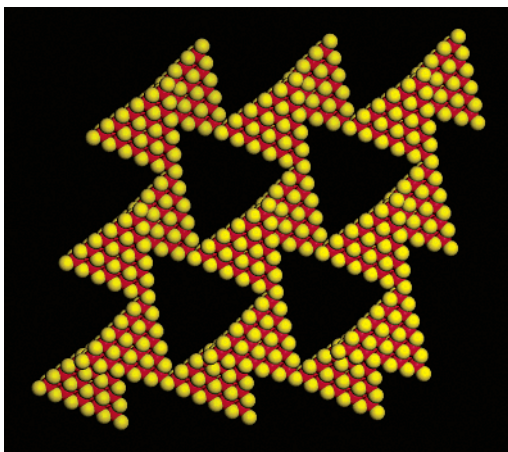


Figure 3. The three-dimensional framework built from T5 supertetrahedral clusters in UCR-17. There are two interpenetrating sublattices, and only one set is shown for clarity.

to-metal distance of about 1.2 nm. The T5 cluster is not only the largest observed supertetrahedral cluster known to date, but it also represents the first supertetrahedral cluster built from tri- and monovalent cations.

Two different superlattices are observed. In both cases, all corners of the T5 cluster are shared through the S^{2-} bridges. UCR-16 has a 2-D chessboard pattern, in which T5 clusters form four-membered rings (i.e., each ring consists of four T5 clusters). UCR-17 has two interpenetrating zinc blende superlattices with six-membered rings. If the number of tetrahedral atoms is used to define the ring size, the ring size for UCR-16 and -17 is 20 and 30, respectively.

In each cluster, the local charge matching surrounding each tetrahedral S^{2-} site is provided by an ordered copper atom at the center of each T5 cluster and a second copper atom located on one of the three supertetrahedral faces adjacent to this tetrahedral S^{2-} site (Figure 1). Because there are four tetrahedral S^{2-} sites per T5 cluster, a total of four copper atoms are distributed among 12 possible metal sites on four supertetrahedral faces. To satisfy Pauling's electrostatic valence rule, each tetrahedral S^{2-} site is surrounded by two Cu^+ and two In^{3+} sites to give a bond valence sum of +2. This leads to an overall formula of $Cu_5In_{30}S_{54}$, consistent with both the elemental analysis¹⁵ and the crystallographic occupancy refinement. The crystallographically determined formula is $Cu_{5.2}In_{29.8}S_{54}$ for UCR-16 and $Cu_{4.8}In_{30.2}S_{54}$ for UCR-17.

As the size of the cluster increases, the pore volume for the guest species also increases. Compared to UCR-5 built from T4 clusters (56% guest space),¹¹ 63% of the crystal volume in UCR-17 is occupied by guest molecules as calculated by the program PLATON.¹⁶ The incorporation of transition metals such as Cu^+ in the T5 cluster may have implications in physical properties of the resulting materials. Indeed, the fluorescent properties of UCR-16 and -17 differ significantly from open framework oxides and chalcogenides reported earlier.^{11,17}

The fluorescent emission in UCR-16 can be excited by a broad solar spectrum from 350 to 630 nm. UCR-16 exhibits two prominent emission peaks at about 540 nm (excited at 350 through 510 nm) and 671 nm (excited at 500 through 630 nm). The fwhm for both

emission peaks is approximately 50 nm. In comparison, previously reported open framework oxides and sulfides typically display only one emission peak that is generally broader (up to 100 nm in fwhm).^{11,17,18} UCR-17 is similar to UCR-16 in the excitation and emission spectra of the 540 nm peak, but the emission at the longer wavelength is less well defined.

In conclusion, the synthesis of UCR-16 and -17 has led to the creation of supertetrahedral clusters with unprecedented size and composition. The global and local charge matching is recognized as an important factor in the formation of these materials. By increasing the size of supertetrahedral clusters, this work represents a step forward toward bridging the size gap between colloidal nanoparticles and small clusters such as T2 and T3.

Acknowledgment. We thank the support of this work by the UC Energy Institute, the donors of the Petroleum Research Fund (administered by the ACS), the National Science Foundation (CHE-0213301), and UC Riverside.

Supporting Information Available: 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) Dance, I.; Fisher, K. In *Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; John Wiley & Sons: New York, 1994; Vol. 41, pp 637–803.
- (2) Krebs, B.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 769–788.
- (3) Bedard, R. L.; Wilson, S. T.; Vail, L. D.; Bennett, J. M.; Flanigen, E. M. In *Zeolites: Facts, Figures, Future. Proceedings of the 8th International Zeolite Conference*; Jacobs, P. A., van Santen, R. A., Eds.; Elsevier: Amsterdam, 1989; p 375.
- (4) Scott, R. W. J.; MacLachlan, M. J.; Ozin, G. A. *Curr. Opin. Solid State Mater. Sci.* **1999**, *4*, 113–121.
- (5) Collier, C. P.; Vossmeier, T.; Heath, J. R. *Annu. Rev. Phys. Chem.* **1998**, *49*, 371–404.
- (6) Soloviev, V. N.; Eichhofer, A.; Fenske, D.; Banin, U. *J. Am. Chem. Soc.* **2001**, *123*, 2354–2364.
- (7) Vossmeier, T.; Reck, G.; Katsikas, L.; Haupt, E. T. K.; Schulz, B.; Weller, H. *Science* **1995**, *267*, 1476–1479.
- (8) Herron, N.; Calabrese, J. C.; Farneth, W. E.; Wang, Y. *Science* **1993**, *259*, 1426–1428.
- (9) Wehmshulte, R. J.; Power, P. P. *J. Am. Chem. Soc.* **1997**, *119*, 9566.
- (10) Li, H.; Kim, J.; Groy, T. L.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2001**, *123*, 4867–4868.
- (11) Wang, C.; Li, Y.; Bu, X.; Zheng, N.; Zivkovic, O.; Yang, C.; Feng, P. *J. Am. Chem. Soc.* **2001**, *123*, 11506–11507.
- (12) Cahill, C. L.; Parise, J. B. *J. Chem. Soc., Dalton Trans.* **2000**, 1475–1482.
- (13) Wang, C.; Bu, X.; Zheng, N.; Feng, P. *J. Am. Chem. Soc.* **2002**, *124*, 10268–10269.
- (14) Hirpo, W.; Dhingra, S.; Kanatzidis, M. G. *J. Chem. Soc., Chem. Commun.* **1992**, 557–558 and references therein.
- (15) Crystallographic data for UCR-16, $(Cu_5In_{30}S_{54})(C_{13}H_{26}N_2H_2)_{6.5}$, $C2/c$, $a = 27.615(9) \text{ \AA}$, $b = 27.648(9) \text{ \AA}$, $c = 28.548(9) \text{ \AA}$, $\beta = 112.761(6)^\circ$, $V = 20099(11) \text{ \AA}^3$, $Z = 4$, Mo $K\alpha$, $T = 150 \text{ K}$, $2\theta_{max} = 40^\circ$, $R(F) = 9.44\%$ for 421 parameters and 3464 reflections with $I > 2\sigma(I)$. Elemental analysis (wt %): 15.34 (calc. 14.76) for C, 2.80 (calc. 2.67) for H, 2.64 (calc. 2.65) for N, 49.17 (calc. 50.11) for In, 4.27 (calc. 4.62) for Cu. Crystallographic data for UCR-17, $(Cu_4.8In_{30.2}S_{54})(C_{13}H_{26}N_2H_2)_{6.5}$, $Fddd$, $a = 43.266(6) \text{ \AA}$, $b = 43.467(6) \text{ \AA}$, $c = 53.721(7) \text{ \AA}$, $V = 101030(23) \text{ \AA}^3$, $Z = 16$, Mo $K\alpha$, $2\theta_{max} = 45^\circ$, $R(F) = 7.35\%$ for 415 parameters and 8812 reflections with $I > 2\sigma(I)$. Electron microprobe elemental analysis (wt %): 48.90 (calc. 50.11) for In, 4.16 (calc. 4.62) for Cu. UCR-17 has a body-centered pseudotetragonal cell with $a = 30.665(3) \text{ \AA}$ and $c = 53.721(7) \text{ \AA}$. In both UCR-16 and -17, all framework atoms are unambiguously located, but amine molecules are disordered.
- (16) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.
- (17) Wang, C.; Bu, X.; Zheng, N.; Feng, P. *Angew. Chem.* **2002**, *41*, 1959–1961.
- (18) Feng, P. *Chem. Commun.* **2001**, 1668–1669.

JA021009Z