Inorganic Chemistry
Article

Inorg. Chem. **2010**, *49*, 8305–8309 **8305**
DOI: 10.1021/ic100688z

New Three-Dimensional Thiostannates Composed of Linked Cu_8S_{12} Clusters and the First Example of a Mixed-Metal Cu_7SnS_{12} Cluster

Malte Behrens,[†] Marie-Eve Ordolff,[†] Christian Näther,[†] Wolfgang Bensch,[†] Klaus-Dieter Becker,[‡] Catherine Guillot-Deudon,[§] Alain Lafond,[§] and Jason A. Cody*[,§,‖]

[†]*Institute of Inorganic Chemistry, Christian-Albrechts-University of Kiel, Max-Eyth-Str. 2, 24118 Kiel, Germany,* [‡]*Technische Universität zu Braunschweig, Braunschweig, Germany,* [§]*Institut des Matériaux Jean Rouxel, UMR 6502 CNRS-Université de Nantes, 2 rue de la Houssinière, BP32229, 44322 Nantes cedex 03, France, and* [‖]*Department of Chemistry, Lake Forest College, 555 N. Sheridan Rd., Lake Forest, Illinois 60045*

Received April 11, 2010

Three new compounds $(enH)_{6+n}Cu_{40}Sn_{15}S_{60}$ (**1**), $(enH)_3Cu_7Sn_4S_{12}$ (**2**), and $(trenH_3)Cu_7Sn_4S_{12}$ (*tren* = tris(2-aminoethyl)-amine) (**3**) containing Cu_8S_{12} and Cu_7SnS_{12} clusters have been prepared from direct solvothermal reaction of the elements in amine solvents. In **1**, the cubic close-packed arrangement of Cu_8S_{12} clusters, interconnected by capping SnS_4 tetrahedra and CuS_3 triangles, form two interpenetrating channel networks that are presumably filled with disordered solvent molecules. Structures **2** and **3** contain well-ordered, protonated amine molecules and Cu_7SnS_{12} clusters. The clusters are connected by SnS_4 tetrahedra to form a three-dimensional structure with ReO_3 topology. ^{119}Sn Mössbauer measurement is consistent with Sn^{IV} atoms *linking*, and Sn^{II} atoms *within*, the mixed-metal Cu_7SnS_{12} clusters.

Introduction

Much recent effort has focused on the search for new inexpensive photovoltaic materials and their synthetic processes so that the costs of widespread solar electricity generation can become more competitive with current fossil fuel technologies.[1,2] Currently most commercial solar cells are composed of abundant, but not-so-cheap-to-process silicon (polycrystalline, amorphous, or single crystal) with quite high conversion efficiencies. Thin-film materials that contain GaAs, CdTe, or chalcopyrite compounds of Cu, In, Ga, S, or Se[3] are expected to be cheaper and have achieved efficiencies up to 20.1%.[4] In particular, compounds such as Cu(In, Ga)S_2 (CIGS) exhibit desirable structural and optoelectronic properties[5] and have even been prepared as nanocrystallites.[6] Already, a few companies have developed large-scale production of modules based on CIGS materials.

Although CIGS materials are efficient absorbers, the increased demand for photovoltaic cells has contributed to a recent drastic increase in the price of elemental indium, a relatively rare element. Thus, one approach to improving single band gap solar cells has recently centered on chemical substitution for indium by less expensive elements, including tin and silicon. In particular, direct solid state reactions have permitted the preparation of $Cu_2Si_xSn_{1-x}S_3$ ($0.4 \leq x \leq 0.6$) compounds that are analogous to $CuInS_2$ with a formula of $Cu(Cu_{1/3}Sn_{1/3}Si_{1/3})S_2$.[7]

More recently, so-called "third generation" solar cells have been proposed with multiple band gap layers and/or nanoparticle composites thereby increasing the efficiency but also increasing both the complexity of the devices and the cost of making them.[8] Because of the desirable optoelectronic properties of the chalcogenide compounds of Group 14/16 elements, several approaches have been explored for intimate combinations of these elements as precursors for the light-absorbing materials in new solar cell designs. First, volatile hybrid compounds for chemical vapor deposition can be prepared via solution-phase coordination chemistry as was first reported for $CuInQ_2$ (Q = S, Se).[9] This has led to a resurgence in thio- and selenocarboxylate metal compounds[10]

---

*To whom correspondence should be addressed. E-mail: cody@lakeforest.edu. Phone: 847-735-5093. Fax: 847-735-6194.

(1) Barnham, K. W. J.; Mazzer, M.; Clive, B. *Nat. Mater.* **2006**, *5*, 161–164.
(2) Goetzberger, A.; Hebling, C.; Schock, H. *Mater. Sci. Eng., R* **2003**, *40*, 1–46.
(3) Miles, R. W.; Zoppi, G.; Forbes, I. *Mater. Today (Oxford, U. K.)* **2007**, *10*, 20–27.
(4) Powalla, M.; Jackson, P.; Lotter, E.; Hariskos, D.; Paetel, S.; Würz, R.; Menner, R.; Wischmann, W. Presented at the E-MRS Spring 2010 Meeting, Strasbourg, France, June 2010.
(5) Compaan, A. D. *Sol. Energy Mater. Sol. Cells* **2006**, *90*, 2170–2180.
(6) Xiao, J.; Xie, Y.; Xiong, Y.; Qian, Y. *J. Mater. Chem.* **2001**, *11*, 1417–1420.
(7) Lafond, A.; Cody, J. A.; Souilah, M.; Guillot-Deudon, C.; Kiebach, R.; Bensch, W. *Inorg. Chem.* **2007**, *46*, 1502–1506.
(8) Conibeer, G. *Mater. Today (Oxford, U. K.)* **2007**, *10*, 42–50.
(9) Hirpo, W.; Dhingra, S.; Sutorik, A. C.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 1597–1599.
(10) Vittal, J. J.; Ng, M. T. *Acc. Chem. Res.* **2006**, *39*, 869–877.

© 2010 American Chemical Society
Published on Web 08/20/2010

and cluster chemistry.[11] Tin/copper/sulfur complexes have been prepared through assembly of copper moieties with $Sn(edt)_2$ (edt = ethane-1,2-dithiolate) to form complexes such as $[Sn_3Cu_4(S_2C_2H_4)_6(\mu_3\text{-O})(PPh_3)_4]^{2+}$,[12] $[(Ph_3P)_2Cu]_2\text{-}SnS(edt)_2$,[13] and $[Sn(edt)_2Cl(\mu\text{-I})(\mu_3\text{-I})(CuPPh_3)_3]$.[14] A second approach to solar cell precursors is solvothermal syntheses of ternary compounds such as $(DBUH)CuSnS_3$ (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene),[15] $(1,4\text{-dabH}_2)Cu_2SnS_4$ (dab = diaminobutane),[15] and $(dienH_2)Cu_2Sn_2S_6$ (dien = diethylenetriamine)[16] that could be thermally decomposed in place to yield the desired ternary absorber materials.

We have prepared three new compounds that are a bridge between the two approaches, combining cluster chemistry and extended structures.[17] The new compounds $(en\text{H})_{6+n}Cu_{40}Sn_{15}S_{60}$ (**1**), $(en\text{H})_3Cu_7Sn_4S_{12}$ (**2**), and $(tren\text{H}_3)Cu_7Sn_4S_{12}$ (*tren* = tris(2-aminoethyl)amine) (**3**) presented herein all contain Cu/Sn clusters capped by bridging $Sn^{IV}S_4$ tetrahedra rather than terminal dithiolate ligands. These SnS_4 groups serve to link the clusters into the observed framework three-dimensional (3D) structures. In addition, compounds **2** and **3** exhibit an unexpected inclusion of a Sn^{II} atom in place of one Cu atom in the cluster thus yielding the first mixed-metal Cu_7SnS_{12} cluster. This is unusual from two perspectives: these compounds exhibit the first mixed metal Cu/Sn sulfur cluster, and these compounds join a small handful of examples in the structurally rich family of thiostannate compounds containing both Sn^{II} and Sn^{IV}.[18–23]

Experimental Section

Syntheses. All three compounds were prepared solvothermally: $(en\text{H})_{6+n}Cu_{40}Sn_{15}S_{60}$ (**1**) and $(en\text{H})_3Cu_7Sn_4S_{12}$ (**2**) were obtained in a single reaction of Cu_2S (134.1 mg, 1.05 mmol), Sn (50.0 mg, 0.42 mmol), and S (30 mg, 0.94 mmol) in 5.0 mL of ethylenediamine. The reaction mixture was heated at 160 °C for 72 h in a 23 mL volume Teflon-lined pressure reactor then removed from the ovens to cool. The product contained low yields of black cubes of (**1**) and red blocks of (**2**) that were manually selected for single crystal X-ray diffraction experiments; although crystals of (**2**) were obtained several times from the same reaction mixture in the same reactors, compound (**1**) was only obtained once. $(tren\text{H}_3)Cu_7Sn_4S_{12}$ (**3**) was synthesized using elemental Cu (63 mg, 1 mmol), Sn (118.9 mg, 1 mmol), and S (96 mg, 3 mmol) in 6 mL 100% tris-(2-aminoethyl)amine. The mixture was heated to 170 °C for 6 d in Teflon-lined steel autoclaves (volume ca. 30 mL) using a diffusion cell where the solid educts are separated by a permeable membrane. The product contained brownish crystals of **3** in a yield of about 25% based on Cu. All three compounds are stable in air for several months.

Table 1. EDX Analysis Results and Refined Structural Occupancies for **1**, **2**, and **3**

structure	analysis	Cu	Sn	S
1	EDX[a]	34.4(1.4)	12.8(2)	52.7(1.3)
	structure	34.8	13.0	52.2
2	EDX	29.7(1)	17.2(2)	53.1(8)
	structure	30.4	17.5	52.2
3	EDX	30.3(2)	17.8(2)	51.8(4)
	structure	30.4	17.5	52.2

[a] Standard deviations for several measurements are given in parentheses.

Table 2. Crystallographic Data for **1**, **2**, and **3**

	1	**2**	**3**
chemical formula	$(C_2H_9N_2)_{6+n}Cu_{40}Sn_{15}S_{60}$	$(C_2H_9N_2)_3Cu_7Sn_4S_{12}$	$(C_6H_{21}N_4)Cu_7Sn_4S_{12}$
a, Å	25.260(4)	13.5317(19)	13.1059(6)
c, Å		28.933(6)	29.347(2)
V, Å^3	16 119(5)	4588.0(13)	4365.4(4)
Z	4	6	6
formula weight, g mol^{-1}	6618.27	1487.60	1451.51
space group	$Pn\bar{3}n$	$R\bar{3}c$	$R3c$
T, °C	−113	−113	293
λ, Å	0.71073	0.71073	0.71073
D_{calcd}	2.727	3.230	3.313
μ, cm^{-1}	8.219	8.800	9.24
$R1(F_o)$[a]	0.0364	0.0368	0.0441
$wR2(F_o^2)$	0.0953	0.0780	0.1159

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma(F_o^2) + (aP)^2 + bP]$ where $P = (\max(F_o^2,0) + 2F_c^2)/3$.

EDX. The chemical compositions of samples **1** and **2** were analyzed using an Energy Dispersive X-ray (EDX)-equipped scanning electron microscope (JEOL 5800LV). These analyses were performed on polished sections of the products imbedded in epoxy; several spots from several crystals were compared to internal standards and averaged. The EDX data for compound **3** (ESEM XL-30, Philips) were acquired on five different crystals. Table 1 summarizes the measured elemental percentages for all three compounds.

X-ray Crystallography. The structures of all three compounds were determined by single crystal X-ray studies. The data collections for **1** and **2** were carried out on a Bruker-Nonius Kappa CCD diffractometer using graphite monochromated Mo K_α radiation. Crystals were mounted on the tip of broken capillary tubes. The data set for compound **3** was collected on an IPDS-1 (STOE) using Mo-K_α radiation. Data collection conditions and X-ray crystallographic details are given in Table 2.

Many crystals of **1** were studied, and all gave comparable structure solutions with the use of the SHELXTL software package.[24] The inorganic portion of the structure is well-behaved and accounts for nearly all of the electron density. Moreover, since the positive charges of the inorganic cations (Cu(I) and Sn(IV)) sum to 40 + 4(15) = 100 but the inorganic anions sum to −120, there must be 20 positive charges from the solvent molecules, only 6 of which are found in the structure. The remaining 14 positive charges must be located on the highly disordered protonated amine molecules within the large cavities. The SQUEEZE function of the PLATON software suite[25] located a void volume of 4343.1 Å^3 in the unit cell volume of

---

(11) Dehnen, S.; Melullius, M. *Coord. Chem. Rev.* **2007**, *251*, 1259–1280.
(12) Wang, X.; Sheng, T.; Fu, R.; Hu, S.; Xiang, S.; Wang, L.; Wu, X. *Inorg. Chem.* **2006**, *45*, 5236–5238.
(13) Wang, L.; Sheng, T.; Wang, X.; Chen, D.; Hu, S.; Fu, R.; Xiang, S.; Wu, X. *Inorg. Chem.* **2008**, *47*, 4054–4059.
(14) Han, Y.; Xu, C.; Duan, T.; Wu, F.; Zhang, Q.; Leung, W. *Inorg. Chem.* **2009**, *48*, 8796–8802.
(15) Pienack, N.; Näther, C.; Bensch, W. *Solid State Sci.* **2007**, *9*, 100–107.
(16) Pienack, N.; Puls, A.; Näther, C.; Bensch, W. *Inorg. Chem.* **2008**, *47*, 9606–9611.
(17) Feng, P.; Bu, X.; Zheng, N. *Acc. Chem. Res.* **2005**, *38*, 293–303.
(18) Ding, N.; Kanatzidis, M. G. *Angew. Chem., Int. Ed.* **2006**, *45*, 1397–1401.
(19) Gressier, P.; Meerschaut, A.; Rouxel, J. *Mater. Res. Bull.* **1987**, *22*, 1573–1580.
(20) Jobic, S.; Le Boterf, P.; Brec, R.; Ouvrard, G. *J. Alloys Compd.* **1994**, *205*, 139–145.
(21) Jobic, S.; Bodenan, F.; Ouvrard, G.; Elkaim, E.; Lauriat, J. P. *J. Solid State Chem.* **1995**, *115*, 165–173.
(22) Cruz, M.; Morales, J.; Espinos, J. P.; Sanz, J. *J. Solid State Chem.* **2003**, *175*, 359–365.
(23) Nayek, H. P.; Massa, W.; Dehnen, S. *Inorg. Chem.* **2008**, *47*, 9146–9148.
(24) Sheldrick, G. M. *SHELXTL Software*, SGI Version; Siemens Analytical X-Ray Instruments, Inc.: Madison, WI, 1997.
(25) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7–13.

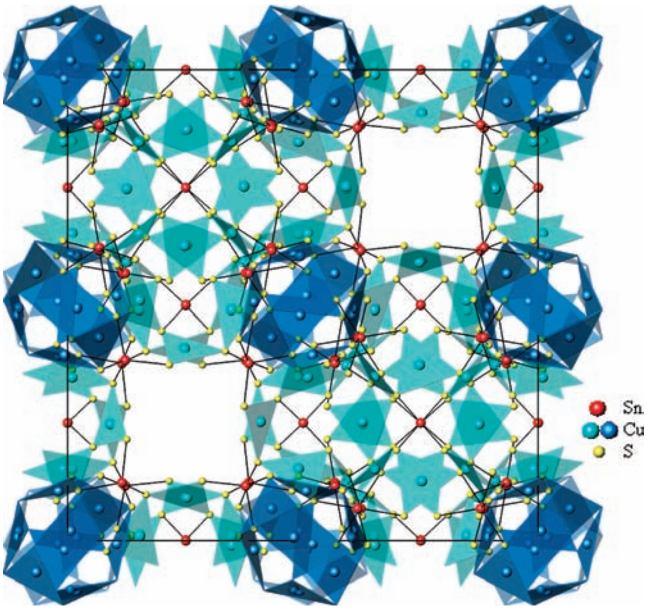

Figure 1. Polyhedral representation of the unit cell of $(en\mathrm{H})_{6+n}\mathrm{Cu}_{40}\mathrm{Sn}_{15}\mathrm{S}_{60}$ (**1**) viewed along the *c* axis. Dark blue CuS_3 triangles are part of the $\mathrm{Cu}_8\mathrm{S}_{12}$ cluster; light blue CuS_3 triangles link clusters. The large open channels contain the highly disordered counterions.

16119 Å^3 (26.9% of total volume). SQUEEZE was used to remove the small amount of residual electron density from the voids. This procedure had little effect on the overall structure refinement, essentially leaving the *R* factors nearly unchanged.

In compounds **2** and **3**, the positional disorder of Sn and Cu in the clusters was refined using a split model with refined occupancies of one Sn atom per $\mathrm{Cu}_7\mathrm{SnS}_{12}$ cluster. The refined occupancies agree well with the EDX measurements (see above).

^{119}Sn Mössbauer Measurements. ^{119}Sn Mössbauer spectrum of $(tren\mathrm{H}_3)\mathrm{Cu}_7\mathrm{Sn}_4\mathrm{S}_{12}$ (**3**) was collected at room temperature. The doublet−doublet fit shows Sn present in two different chemical environments: Sn(1) corresponds to a highly symmetrical (tetrahedral) $\mathrm{Sn}^{\mathrm{IV}}$ atom; Sn(2) shows greater quadrupolar splitting and higher center shift consistent with $\mathrm{Sn}^{\mathrm{II}}$. Isomer shifts of ^{119}Sn are relative to BaSnO_3 with source and absorber at ambient temperatures.

Results and Discussion

All three compounds consist of an anionic skeleton formed of Sn, Cu, and S atoms; voids in the structures are occupied by protonated amine molecules that are disordered in **1** and well-ordered in **2** and **3**. The large cubic unit cell of **1** (Figure 1) shows a complex connectivity of CuS_3 triangles and SnS_4 tetrahedra. $\mathrm{Cu}_8\mathrm{S}_{12}$ clusters (Figure 2a), composed of vertex-linkage of CuS_3 triangles, are located at the center of all edges and faces (ccp arrangement) and are capped by six SnS_4 units that each form links to six other $\mathrm{Cu}_8\mathrm{S}_{12}$ clusters through additional bridging CuS_3 groups (Figure 2b). Additional pendant CuS_3 and a SnS_4 group complete the structure forming two interpenetrating channel networks (Figure 2c). The $\mathrm{Sn(2)S}_4$ tetrahedron is joined to 8 CuS_3 triangles, that is, each S atom is μ_3-bridging. The $\mathrm{Sn(1)S}_4$ tetrahedron is also surrounded by 8 CuS_3 groups but in a different connection mode because one S atom is μ_4-connecting whereas a second S acts in a μ_2-mode. Cu−Cu distances in the cube are longer than 3 Å and are thus too long for bonding interactions[26] (see Table 3). The

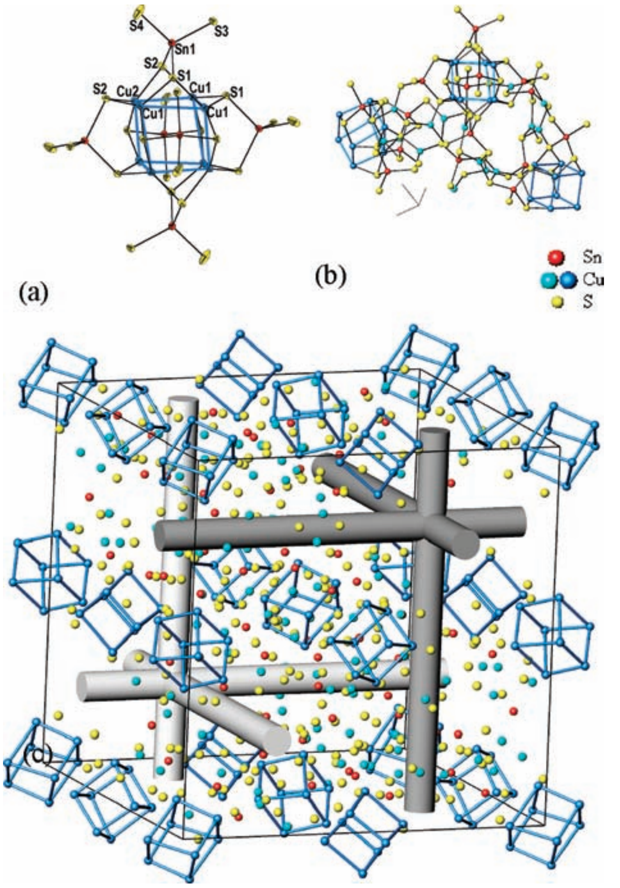

Figure 2. (a) $\mathrm{Cu}_8\mathrm{S}_{12}$ cluster from **1** (atoms as 50% thermal ellipsoids; blue lines emphasize the cube, not Cu−Cu bonds); (b) The same $\mathrm{Cu}_8\mathrm{S}_{12}$ cluster from **1** shown nestled in its context of linking SnS_4 tetrahedra and CuS_3 triangles. Only two of the six adjacent clusters are shown. (c) The light and dark gray cylinders illustrate the two distinct channel networks through the structure.

CuS_3 triangles display different amounts of distortion with S−Cu−S angles ranging from 107.5 to 133.7°.

The $\mathrm{Cu}_8\mathrm{S}_{12}$ clusters found in **1** resemble several molecular $\mathrm{Cu}_8\mathrm{S}_{12}$ clusters that were synthesized through solution-phase reactions.[26−28] In these discrete, molecular species, each face of the Cu_8 "cube" is capped by a terminal dithiolate ligand such that each Cu atom is coordinated to three S atoms in nearly trigonal planar geometry.

Although one well-ordered ethylenediamine molecule was located in a minor side channel of **1** with hydrogen bonding to nearby S atoms, very little order in electron density can be found in the large voids that form the interpenetrating channel networks. The disorder in the voids does not come from the artificially high pseudosymmetry of the inorganic substructure. Unfortunately, because of the very small amount of sample obtained, further chemical analyses were not possible to confirm the presence of protonated amines in the voids. However, using the simple rule of thumb that one non-hydrogen atom occupies approximately 20 Å^3, the volume of Cu, Sn, and S atoms in one unit cell (four $(en\mathrm{H})_{6+n}\mathrm{Cu}_{40}\mathrm{Sn}_{15}\mathrm{S}_{60}$ units) is 11120 Å^3, in good agreement with the non-void volume calculated by SQUEEZE (11775 Å^3). If the

---

[26] Hollander, F. J.; Coucouvanis, D. *J. Am. Chem. Soc.* **1977**, *99*, 6268–6279.

[27] Behrens, M.; Scherb, S.; Näther, C.; Bensch, W. *Z. Anorg. Allg. Chem.* **2003**, *629*, 1367–1373.

[28] Dietrich, H.; Storck, W.; Manecke, G. *Makromol. Chem.* **1981**, *182*, 2371–2398.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **1**, **2**, and **3**

	1	**2**	**3**
chemical formula	$(C_2H_9N_2)_{6+x}Cu_{40}Sn_{15}S_{60}$	$(C_2H_9N_2)_3Cu_7Sn_4S_{12}$	$(C_6H_{19}N_4)Cu_7Sn_4S_{12}$
$Sn^{IV}-S$	2.380(2)−2.410(1)	2.407(2)−2.423(2)	2.390(4)−2.423(4)
$Sn^{II}-S$		2.676(2)−2.706(2)	2.657(4)
Cu−S	2.230(1)−2.273(1)	2.246(1)−2.287(1)	2.235(5)−2.322(4)
Cu−Cu	3.021(1)	3.047(1)	3.032(3)
S−Cu−S	107.5(1)−133.7(1)	112.6(1)−126.8(1)	113.6(2)−126.5(2)
$S-Sn^{IV}-S$	104.5(1)−113.0(1)	105.5(1)−114.1(1)	104.8(1)−112.6(2)
$S-Sn^{II}-S$		88.9(1)−94.7(1)	88.0(1)

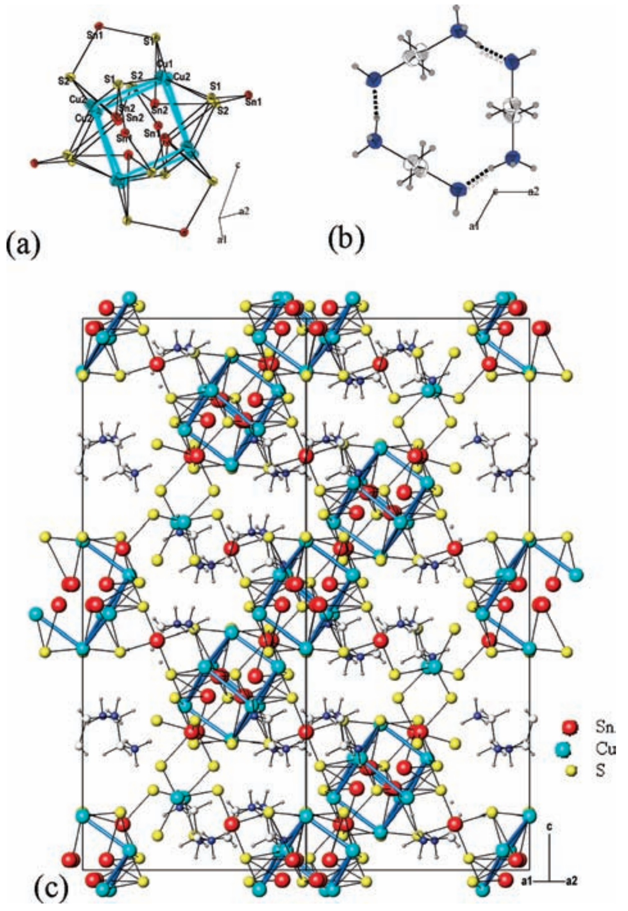

Figure 3. (a) Cu_7SnS_{12} cluster and (b) ring of three protonated *en* molecules from $(en\text{H})_3Cu_7Sn_4S_{12}$ (**2**) (atoms as 50% thermal ellipsoids; blue lines emphasize the cube, not Cu−Cu bonds); (c) Unit cell of **2**. Within the Cu_7Sn clusters, there is one Sn atom disordered over six symmetrically equivalent sites. Since there cannot be an Sn atom and a Cu atom simultaneously present in the same corner of the cluster, the occupancy of Sn was constrained to 1/6 and the occupancy of Cu was constrained to 5/6, in accordance with the careful EDX measurements (see Table 1). The unit cell of $(tren\text{H}_3)Cu_7Sn_4S_{12}$ (**3**) is very similar to the one shown above with inclusion of only one Sn site within the Cu_7Sn clusters and substitution of one triply protonoated *tren* molecule in place of three protonated *en* molecules.

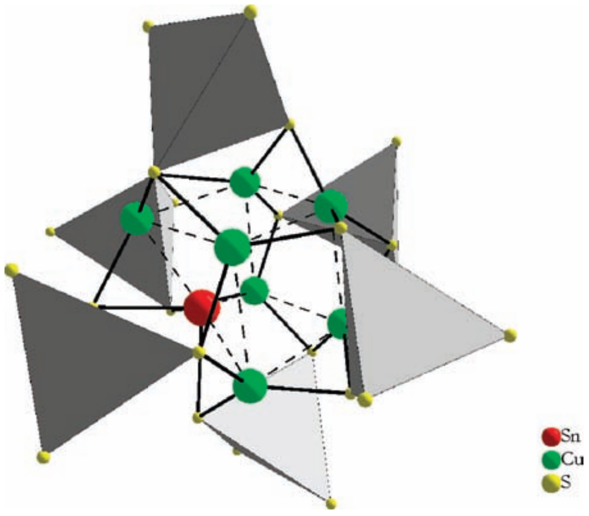

Figure 4. Polyhedral representation of the chemically modified Cu_7SnS_{12} clusters found in **2** and **3**. One Sn atom is disordered over 6 equivalent sites in **2**; there is no disorder in **3**. Dotted lines between copper atoms are drawn to emphasize the arrangement, but the > 3 Å separation is too long for Cu−Cu bonding.

six well-behaved *en* molecules are monoprotonated, then there should be the equivalent volume of 14 more monoprotonated *en* molecules for charge balance (the sum of 40 Cu(I) plus 15 Sn(IV) is 100 positive charges; the 60 S(-II) ions give −120 or an excess of 20 negative charges). If one divides the void volume of 4343 Å^3 by Z, then divides again by the roughly 80 Å^3 per *en* molecule, one obtains a void volume equivalent to 13.5 *en* molecules—in good agreement with the 14 missing positive charges.

The unit cells of **2** and **3** (Figure 3) contain chemically modified Cu_7SnS_{12} clusters (see Figures 3a and 4) that are linked by six bridging SnS_4 tetrahedra to form the overall 3D structure; superoctahedra drawn with Sn atoms at all vertices form a three-dimensional network through corner-sharing and give rise to solvent-filled channels running along [100], [010], and [110] resembling the ReO_3 structure type. The dimensions of the channels are about 8.6 × 8.6 Å (measured from atom center to atom center).

Unlike structure **1**, the solvent molecules are highly ordered in structures **2** and **3**. For example, in **3** two of the H atoms of the protonated N atoms have relatively short contacts to S atoms of the Cu_7SnS_{12} clusters (S···H: 2.364 and 2.654 Å with corresponding N−H···S of 161.0 and 149.1°). Such hydrogen bonding interactions may be responsible for the high order of the structure directing molecules.

The observed bond lengths and angles are similar to other known thiostannates. The Sn−S bond lengths in the linking $Sn^{IV}S_4$ tetrahedra range from 2.380(2)Å to 2.427(4)Å with corresponding S−Sn−S angles between 104.5(1)° and 114.1(1)°; they are within the normal range and indicate a moderate distortion. The S−S bite distances of bridging thiolate ligands found in known discrete molecular Cu_8 compounds (i.e., 3.92 Å)[26] are similar to the S−S bite distances of the SnS_4 tetrahedra in the current compounds (3.81 Å in **1** and 3.85 Å in **2**). In **2** and **3**, the Sn atom of the Cu_7Sn cluster is in a trigonal-pyramidal environment of three S atoms at 2.680(4)−2.788(4) Å and 2.651(4) Å, respectively.

The trigonal-pyramidal environment of S atoms for a Sn atom was recently observed in $(DBNH)_2Sn_3S_6$ (DBN = 1,5-diazabicyclo[4.3.0]non-7-ene) with $Sn^{II}-S$ bond length between 2.5059(13) and 2.5511(17) Å.[29] There are some other

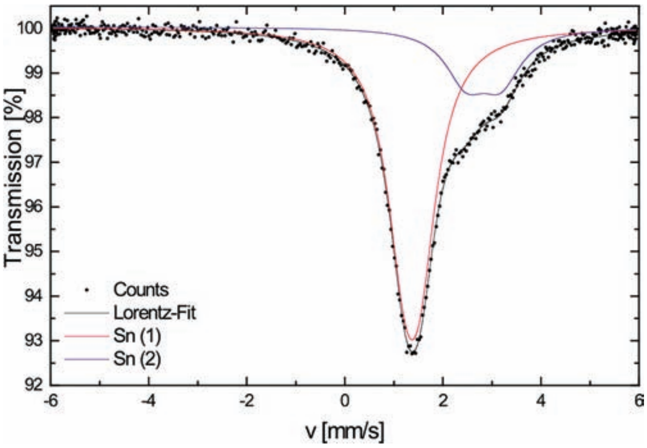

Figure 5. ^{119}Sn Mössbauer spectrum of $(tren\mathrm{H}_3)\mathrm{Cu}_7\mathrm{Sn}_4\mathrm{S}_{12}$ (**3**) collected at room temperature. The doublet−doublet fit shows Sn present in two different chemical environments: Sn(1) corresponds to a highly symmetrical (tetrahedral) Sn^{IV} atom; Sn(2) shows greater quadrupolar splitting and higher center shift consistent with Sn^{II}. Isomer shifts of ^{119}Sn are relative to $BaSnO_3$ with source and absorber at ambient temperatures.

examples with SnS_3 pyramids like Ottemannite,[30] $C_{25}H_{27}NO_3SnS_3$,[31] $C_{42}H_{35}AsSnS_3$,[32] and $C_{42}H_{35}PSnS_3$[33] in which the Sn−S bonds range between 2.532(10) and 2.765(2) Å. Hence, compounds **2** and **3** are rare examples of the presence of SnS_3 pyramids and the coexistence of Sn^{II} and Sn^{IV} centers. It is highly likely that the lone electronic pair of Sn^{II} points toward the middle of the cluster.

The presence of both Sn^{II} and Sn^{IV} in **3** was confirmed by Mössbauer spectroscopy. In the spectrum (Figure 5) the two observed signals are best fitted with two doublets. The isomer shift δ of the first peak is 1.37 mm/s and for the second peak δ is 2.83 mm/s. The value for the quadrupole splitting ΔE_Q is 0.31 mm/s for the first Sn species and 0.71 mm/s for the second species. The relative area of the two peaks is 76:24, which is very near 3:1 expected from the structure that contains three $\mathrm{Sn}^{IV}\mathrm{S}_4$ linking tetrahedra for every Sn^{II} in the bimetallic cluster. The isomer shift of species 1 agrees with the Sn^{IV} oxidation state and is identical with that of SnS_2 (1.3 mm/s).[34] The small value of ΔE_Q indicates a slight distortion of the SnS_4 tetrahedron and is consistent with the geometric data. The value for δ of the second species is between that of SnO (2.64 mm/s) and SnS (3.38 mm/s),[34] that is, in the range of divalent Sn. The larger ΔE_Q for this Sn atom can be explained by the unsymmetrical environment of S atoms. The Cu−Cu distances in the Cu_7Sn cluster are longer than 3 Å, whereas the Cu−Sn separation of 2.607 Å−2.648 Å in **2** and 2.731 Å in **3** is of the order found in bronze (2.519 Å and 2.728 Å[35]). In addition bond valence sum calculations for **2** and **3** are in full agreement with the presence of Sn^{II} and Sn^{IV}.

The solvothermal chemistry of copper, tin, and sulfur remains quite rich for further study since it provides a bridge between solution-phase, copper−sulfur cluster chemistry, and extended, 3D materials chemistry, both of which provide possible routes to absorber materials for third generation solar cells. This combination of elements is very attractive because it has both desirable photovoltaic properties and relatively abundant and inexpensive elements.

Conclusions

The three new copper−tin−sulfur compounds with framework 3D structures presented herein expand upon the well-developed solution-phase chemistry of Cu_8S_{12} cubes and provide a possible starting material for photovoltaic absorber materials. New materials like these can provide routes to the desired costs and optical efficiencies required by advanced solar cell technologies. All three compounds incorporate bridging SnS_4 tetrahedra in place of terminal organic dithiolate ligands, thus building the interconnected 3D structures. Moreover, the observed Cu_7SnS_{12} clusters prepared in situ are the first examples of such mixed-metal groups in Cu_8 cluster chemistry and include Sn^{II} inside the clusters and Sn^{IV} linking the clusters. At present, the relatively low yields of all three compounds prevent decomposition experiments and further characterizations, but optimization of the syntheses are underway to increase the yields for future experiments.

Acknowledgment. J.A.C. thanks Lake Forest College and the University of Nantes for his research sabbatical.

Supporting Information Available: CIF files and bond valence calculation results. This material is available free of charge via the Internet at http://pubs.acs.org.

---

(29) Pienack, N.; Näther, C.; Bensch, W. *Eur. J. Inorg. Chem.* **2009**, 937–946.

(30) Kniep, R.; Mootz, D.; Severin, U.; Wunderlich, H. *Acta Crystallogr., Sect. B* **1982**, *38*, 2022.

(31) Vittal, J. J.; Dean, P. A. W. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1996**, *52*, 1180.

(32) Dean, P. A. W.; Vittal, J. J.; Payne, N. C. *Can. J. Chem.* **1985**, *63*, 394.

(33) Barone, G.; Hibbert, T. G.; Mahon, M. F.; Molloy, K. C.; Parkin, I. P.; Price, L. S.; Silaghi-Dumitrescu, I. *J. Chem. Soc., Dalton Trans.* **2001**, 3435.

(34) Lippens, P. E. *Phys. Rev. B* **1999**, *60*, 4576–4586.

(35) Gangulee, A.; Das, G. C.; Beyer, M. B. *Metall. Trans.* **1973**, *4*, 2063–2066.