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Article

Two-Dimensional Indium Sulfide Framework Constructed from Pentasupertetrahedral P1 and Supertetrahedral T2 Clusters

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A new open-framework indium sulfide ($[In_{12}S_{24}H_2]^{10-}$) constructed from pentasupertetrahedral sulfide clusters ($[In_8S_{17}H],^{9-}$ P1) and supertetrahedral sulfide clusters ($[In_4S_{10}H],^{7-}$ T2) has been prepared through hydrothermal synthesis. Unlike previously reported P1 clusters that require divalent metal cations, the P1 cluster reported here consists of only trivalent ions (In^{3+}) and is the only known example of tetrahedral clusters with a core sulfur site bonded to four trivalent ions. Each P1 cluster is joined to three T2 clusters (vice versa) to form an infinite two-dimensional sheet stacked along the crystallographic *c*-axis. In contrast with known three-dimensional open-framework indium sulfides in which locations of extraframework amines are rarely known due to disorder, structure-directing amine molecules are much less disordered as a result of host–guest N–H···S hydrogen bonding. The UV–vis diffuse reflectance spectrum shows that this material is a wide band gap semiconductor.

Introduction

Over the past decade, a lot of studies have been done in the field of open-framework metal chalcogenides due to their potential applications as porous semiconductors, photocatalysts, etc.[1–8] Unlike many oxide open-framework materials, open-framework chalcogenides frequently consist of clusters as their structural building units. Among various clusters, tetrahedron-shaped clusters have attracted lots of interest in part because they can serve as artificial tetrahedral atoms to form zeolite-like porous semiconductors. Tetrahedral clusters have been classified into three different series: supertetrahedral clusters denoted as T*n*, capped supertetrahedral clusters denoted as C*n*, and pentasupertetrahedral clusters denoted as P*n*.[4] These clusters can be assembled into open-frameworks through inorganic bridges (e.g., S^{2-}) or organic ligands.[9,10]

While the geometrical relationships among these series of clusters are well understood, the chemical relationship is little known. For example, it is not clear whether clusters of different series are interconvertible in a given hydrothermal system, despite their simple geometric relationship. It was suggested earlier that clusters of various types and sizes could coexist in a solution under solvothermal and hydrothermal systems.[4] Equilibria between various clusters in solution would shift to favor one or more clusters when crystallization involving these clusters occurs. The study of known open-framework chalcogenides made of clusters from the same series but with different sizes provides a strong support for the existence of such chemical equilibria between clusters of the same series. For example, in the gallium sulfide system, it is possible to selectively grow open-framework chalcogenides from T3 clusters only ($Ga_{10}S_{20}^{10-}$), T4 clusters only ($Zn_4Ga_{16}S_{35}^{14-}$), or a combination of T3 and T4 clusters.[11]

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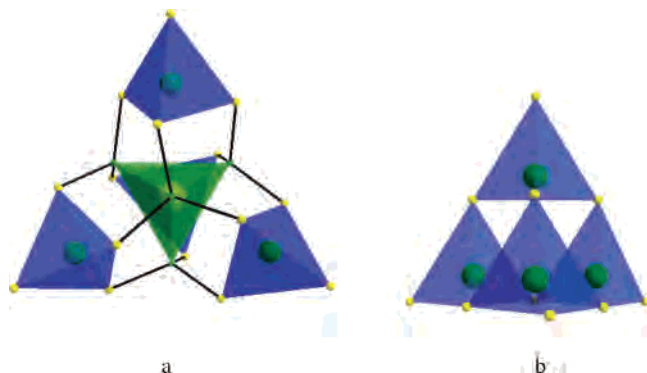† University of California.
‡ California State University.

Figure 1. The structures of (a) the P1 cluster and (b) the T2 cluster (blue tetrahedra: InS_4; green tetrahedron: SIn_4; green ball: In^{3+}; yellow ball: S^{2-}).

In comparison, open-framework chalcogenides consisting of clusters from two different tetrahedral series (mixed frameworks) are very rare.[12] Such mixed frameworks are of particular interest because in addition to their potential applications as porous semiconductors, they may offer insight into the formation mechanism of chalcogenide open-frameworks.

In our continued effort to develop new chalcogenide clusters and their open-frameworks for potential applications,[13,14] we have been examining the use of two different structure-directing agents on the crystallization behaviors of chalcogenide clusters. Here, we report a new two-dimensional indium sulfide framework $[In_8S_{13}(S_3)_{1/2}(SH)][In_4S_6-(S_3)_{1/2}(SH)](TMDPH_2)_5$ (denoted as HCF-1, HCF = hybrid chalcogenide framework; $TMDPH_2$ = diprotonated 4,4′-trimethylenedipiperidine, $C_{13}H_{26}N_2H_2$) constructed from pentasupertetrahedral sulfide clusters (P1, Figure 1a) and supertetrahedral sulfide clusters (T2, Figure 1b).

Experimental Section

Synthesis. To prepare crystals of HCF-1, indium metal (Aldrich, 99.99%, 0.1194 g, 1.04 mmol), sulfur (Alfa Aesar, 99.5%, 0.1985 g, 6.19 mmol), triethylenetetraamine (TETA, Acros, 95%, 0.5015 g, 3.26 mmol), 4,4′-trimethylenedipiperidine (TMDP, TCI, 99.4%, 0.5038 g, 2.39 mmol), and distilled water (3.9092 g, 217.18 mmol) were mixed in a 23 mL Teflon-lined stainless steel autoclave, and the mixture was stirred for 30 min. The vessel was sealed and heated at 150 °C for 5 d. The autoclave was subsequently allowed to cool to room temperature. The hexagonally shaped colorless platelike crystals were obtained with 65% yield. Elemental Analysis: C 24.36%, H 4.26%, N 4.34%, Calc.: C 24.31%; H 4.46%, N 4.36%.

Single-Crystal Structure Analysis A crystal was glued to a thin glass fiber with epoxy resin and mounted on a Bruker APEX II diffractometer equipped with a fine focus, 2.0 kW sealed tube X-ray source (MoKα radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 30 mA. The empirical absorption correction was based on equivalent reflections, and other possible effects such as absorption by the glass fiber were simultaneously corrected. The structure was solved by direct methods followed by successive difference Fourier methods. Because of the positional and orientational flexibility,

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Table 1. Summary of Crystal Data and Refinement Results

name	HCF-1
formula	$In_{12}S_{24}C_{65}H_{142} N_{10}$
size (mm)	$0.22 \times 0.20 \times 0.13$
temp (K)	298
a (Å)	16.2027(3)
c (Å)	25.0578(10)
V (Å^3)	5697.0(3)
Z	2
space group	$P31c$
$2\theta_{max}$ (deg)	45
total data	31706
unique data	4859
data, $I > 2\sigma(I)$	3774
parameters	309
$R(F)$ (%) $(I > 2\sigma(I))$	5.15
$R_w(F^2)$ (%)$(I > 2\sigma(I))$	12.8
GOF	1.04

positions and associated bond lengths of extraframework carbon and nitrogen atoms were less accurately determined. Computations were performed using SHELXTL, and final full-matrix refinements were against F^2. The crystallographic results are summarized in Table 1.

Thermal Analysis. The simultaneous DSC-TGA thermal analysis was performed on TA Instruments SDT Q600. The sample was prepared by grinding single crystals into fine powder. A total of 7.0710 mg was heated between room temperature and 800 °C at a heating rate of 4 °C/min under the static air.

Results and Discussion

One of the most interesting features in HCF-1 is that it has two different types of cluster units: P1 and T2. The P1 cluster is the first member of a series of pentasupertetrahedral clusters (the P*n* series), whereas the adamantane-shaped T2 cluster is the second member in a series of supertetrahedral clusters (the T*n* series).

The pentasupertetrahedral cluster can be conceptually constructed by coupling four supertetrahedral clusters onto each face of an antisupertetrahedral cluster of the same order. An antisupertetrahedral cluster (T-*n*) is defined here as having the same geometrical feature as that of a supertetrahedral cluster (T*n*) with positions of cations and anions being exchanged. Thus the P1 cluster consists of four T1 clusters (MX_4) at corners and one anti-T1 cluster (XM_4) at the core, resulting in the composition of $(MX_4)_4(XM_4)$ (i.e., M_8X_{17}).

In HCF-1, the chemical formula for discrete P1 and T2 clusters is $[In_8S_{17}]^{10-}$ and $[In_4S_{10}]^{8-}$ respectively. In the T2 cluster, nine sulfur sites are coordinated to two In^{3+} sites, while one corner sulfur site is terminated as a −SH group. The −SH group has also been found in other open-framework indium sulfides such as $[C_6H_{16}N]_4In_4S_{10}H_4$ and $(DEA-H)_7{}^+In_{11}S_{21}H_2$.[7,15]

Of the nine sulfur sites, three are corner sites that are shared between two adjacent clusters. Therefore, the T2 cluster in the framework is written as $[In_4S_6(S_3)_{1/2}(SH)]^{4-}$. For the same reason, the P1 cluster is written as $[In_8S_{13}(S_3)_{1/2}-(SH)]^{6-}$. The P1 cluster consists of a core SIn_4 unit surrounded by four InS_4 units and can also be written as $[(SIn_4)(InS_3S_{1/2})_3(InS_3)SH)]^{6-}$ to more accurately reflect its structure and bonding pattern. It is worth noting that in the T*n* series, tetrahedrally bonded sulfur sites only start to occur

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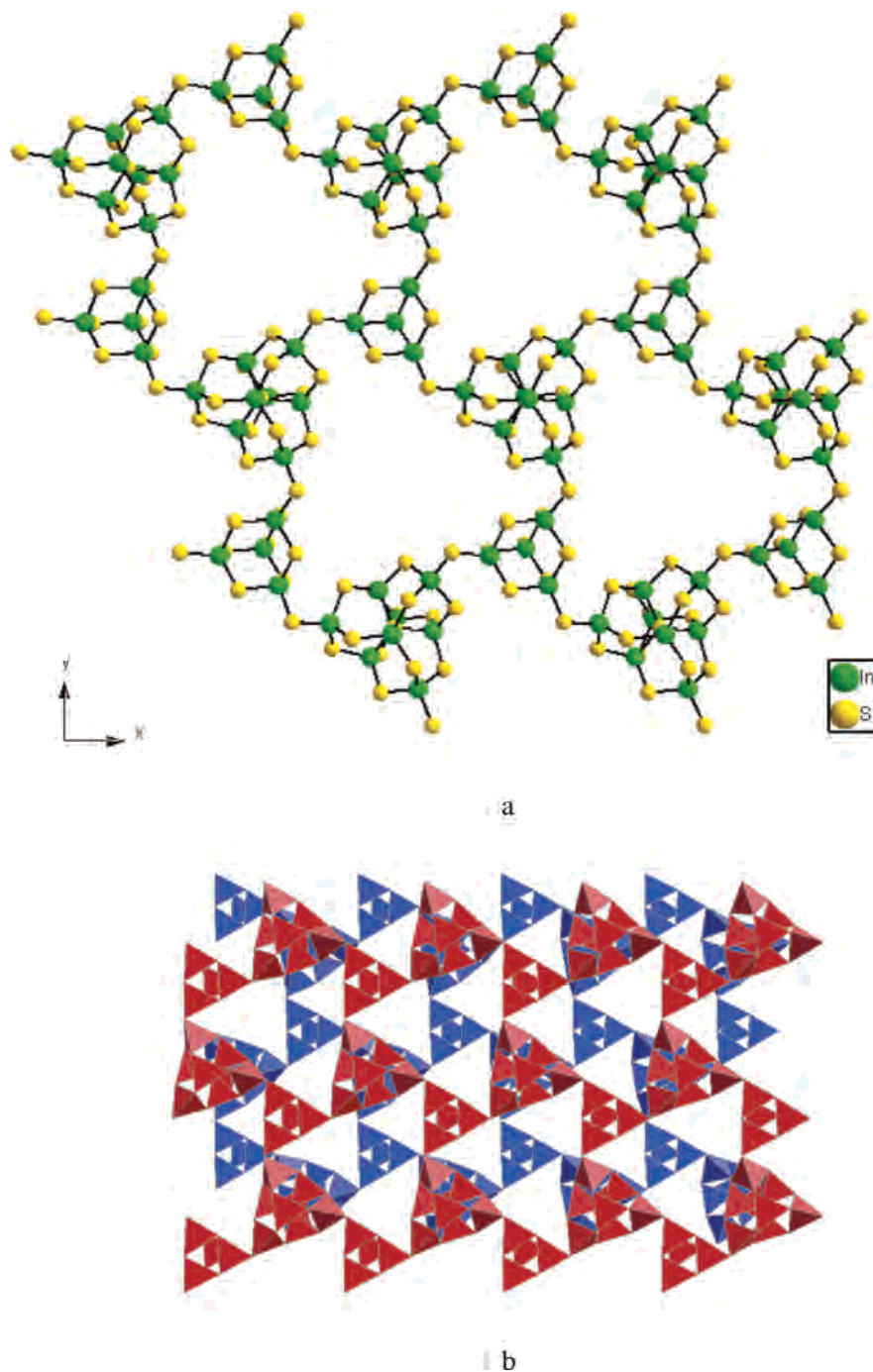
Figure 2. (a) Alternating P1-T2 clusters in HCF-1 (green ball: In; yellow ball: S) and (b) two adjacent layers (represented as blue and red) stacked along the crystallographic c-axis.

with the T4 cluster, whereas in the Pn series, it is present even in the first member (P1).

Within each layer, alternating P1 and T2 clusters are linked together by bridging sulfide atoms (Figure 2a). Each window consists of three P1 clusters and three T2 clusters with a total of 15 tetrahedral indium sites (Figure 2a). These layers are stacked along the c-axis. T2 clusters in one layer are located above or below the center of 15-ring-window of its adjacent layers (Figure 2b), and P1 clusters are located above or below P1 clusters of adjacent layers.

Unexpectedly, P1 clusters were built from trivalent metal cations (i.e., In^{3+}) with the core sulfur site bonded to four

In^{3+} sites. To our knowledge, no known tetrahedral cluster from the three series (Tn, Cn, and Pn) possesses this unusual feature even though examples of the SIn$_4$ unit are known in other types of structures.[16] All previously known P1 clusters require divalent metal cations surrounding the core S^{2-} sites. Examples of these P1 clusters include [SCd$_8$(SBu)$_{12}$(CN)$_{4/2}$],[17] [Cd$_8$E(E′Ph)$_{16}$]$^{2-}$ (E=S, E′=S, Se, Te or E=Se, Te, E′=Se),[18]

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$[Cd_8E(E'Ph)_{12}X_4]^{2-}$ (E=E'=S, X=Cl or E=S, E'=Se, X=Br, I),[18] $M_8S(SPh)_{14}L_2$ (M=Cd, Zn),[9,10] $[Zn_8S(SCH_2C_6H_5)_{16}]^{2-}$,[19] $[M^{II}_4M_4S_{17}]^{10-}$ (M^{II}=Zn, Cd, Fe, Co; M=Sn, Ge),[12,20−21] and $[Sn_4M^{II}_4Se_{17}]^{10-}$ (M^{II}=Co, Zn, Mn, Cd, Hg).[22−25]

It has been generally assumed that monovalent or divalent metal cations are necessary to construct chalcogenide tetrahedral clusters with tetrahedrally bonded sulfur sites because a regular SIn_4 unit would be unstable due to the excessive bond valence from four In^{3+} sites to the central S^{2-} sites. In this particular case, however, the observed In−S bond length (2.614 Å × 2 and 2.546 Å × 2) is significantly longer than the normal In−S bond length (2.44 Å), which led to a significant decrease in the electrostatic bond valence for all four In−S bonds. Using Brown's bond valence model,[26−28] the valence sums surrounding the core S^{2-} site is 2.28 instead of 3 as derived from Pauling's electrostatic valence rule.

Experiments conducted so far show that HCF-1 cannot be synthesized in the absence of TMDP. The presence of TMDP molecules is confirmed by crystal structure analysis and elemental analysis. The second amine, TETA, however, is not encapsulated within the HCF-1 framework on the basis of crystallographic and elemental analysis. The elemental analysis gives a C to N molar ratio of 6.55 that agrees well with the C to N ratio in TMDP (6.5 for $C_{13}H_{26}N_2$) and is much higher than the C to N ratio in TETA (1.5 for $C_6H_{18}N_4$). In addition, HCF-1 can be synthesized when TETA is replaced by other amines such as 1,4-bis(3-aminopropyl)piperidine (BAPP), 1,4-diazabicyclo[2,2,2]-octane, and N,N,N′-trimethylethylenediamine. It is worth noting that the present experimental results show that the presence of a second amine is needed for the synthesis of HCF-1 even though it is not encapsulated into HCF-1. The precise role of the second amine in the formation of HCF-1 remains unclear.

Sixty percent of TMDP molecules are found at one general crystallographic position. Twenty percent of TMDP molecules are located near the crystallographic 3-fold axis and are thus statistically distributed equally among three equivalent positions. The position of the remaining 20% of TMDP molecules cannot be located. The crystallographic order of most TMDP molecules is related to the relatively strong host−guest interactions in the form of electrostatic forces and hydrogen bonding. The distance between N (in TMDP) and S (in P1 clusters) atoms ranges from 3.208 to 3.293 Å,
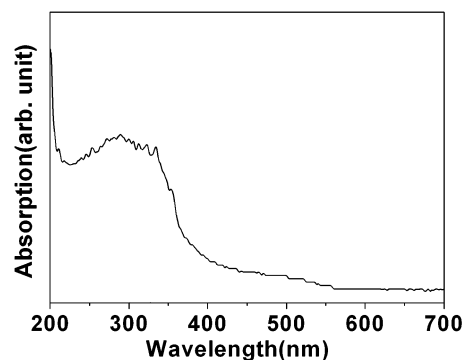

Figure 3. The UV absorption spectrum of HCF-1.

which suggests the presence of the N−H···S bonding. Such N−H···S bonding has rarely been observed in three-dimensional open-framework indium sulfides, and amine molecules in them tend to be completely disordered.

The diffuse reflectance spectrum of HCF-1 was measured on a Shimadzu UV-3101PC double-beam, double-mono-chromator spectrophotometer by using $BaSO_4$ powder as 100% reflectance reference. As shown in Figure 3, optical absorption data derived from the reflectance showed that HCF-1 is a wide gap semiconductor with absorption band edge at 400 nm (3.1 eV) accompanied by a shoulder up to 500 nm (2.5 eV).

The thermogravimetric analysis in the static air showed an initial weight loss of 2.5% between room temperature and 110 °C, likely due to the desorption of surface-adsorbed species (e.g., H_2O). A sharp weight loss of 19.7% was observed between 220 and 300 °C, followed by a second weight loss of 23.6% between 480 and 540 °C. No further weight loss was observed after 540 °C. The final residue was identified to be In_2O_3 by X-ray powder diffraction. The total observed weight loss (43.3%) between 200 and 800 °C is in reasonably good agreement with the calculated weight loss of 48.1%.

In conclusion, a new hybrid framework based on P1 $[In_8S_{13}(S_3)_{1/2}(SH)]^{6-}$ and T2 $[In_4S_6(S_3)_{1/2}(SH)]^{4-}$ clusters have been synthesized. Its structure and optical property have been characterized. The structure represents a rare example of chalcogenide open-framework materials that contain tetrahedral clusters from two different series. Furthermore, the observation of the rare occurrence of the In_4S unit at the center of the P1 cluster demonstrates new possibilities in the development of open-framework chalcogenides. This work represents an interesting development in the synthesis and structural properties of open-framework chalcogenides from hydrothermal systems.

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.

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