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Mixed pentasupertetrahedral P1 and supertetrahedral T2 clusters as building units to create two-dimensional indium chalcogenides open framework

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ABSTRACT

A new two dimensional open framework indium chalcogenide $[In_{12}S_{21}(Se)_3H_2]$, NCYU-5, constructed from pentasupertetrahedral P1 clusters, $[In_8S_{14}(Se_{1/2})_3H]$, and supertetrahedral T2 clusters, $[In_4S_7(Se_{1/2})_3H]$, has been prepared through hydrothermal method. Each T2 cluster is jointed with three P1 clusters via Se atoms to form an infinite two dimensional structure stacked along the crystallographic c axis. The ion-exchange studies show that the guest molecules (TMDP) can be exchanged by monocations (Na^+, K^+), and dications (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}). In the typical exchanged solids by Ba^{2+} cations, the quantitative microanalysis data for the atomic ratio (Ba/Se) of Ba (1.86%) and Se (15.42%) is 12.05%. The luminescent output from the NCYU-5 cluster exhibits a temperature-dependent shift. A shift from $\lambda_{max} = 433$ nm to $\lambda_{max} = 450$ nm occurs as temperature increases from 77 K to 298 K.

Over the past few decades, because of using clusters as structural building units to create their open frameworks, the metal chalcogenides have attracted considerable interest due to their possible applications as porous semiconductors, and fast ion conductors [1–4]. Among these clusters, only the tetrahedral clusters can serve as artificial tetrahedral atoms, and assemble into porous open-framework through inorganic chalcogenide ligands [4,5]. The tetrahedral clusters are classified into three series. They are supertetrahedral clusters (T*n*), capped supertetrahedral clusters (C*n*), and pentasupertetrahedral clusters (P*n*) [3–5]. Although geometrical relationship among same series clusters is well developed [1,5–7], the inter-convertibility between different series clusters in a given hydrothermal reaction is not clear. Nevertheless, open framework chalcogenides consisting of two different tetrahedral series with mixed frameworks, such as a framework mixed with Tn series and Pn series, are very rare [8,9]. In general, when crystallization is involved in the cluster reaction, the equilibria between various clusters shift to the direction to create more clusters [4]. Thus, the coexistence of various types and sizes of clusters in a given hydrothermal system is possible. The mixed framework structure by various series clusters offers a desired chance to examine the formation mechanism of chalcogenide frameworks in addition to the potential application in porous semiconductors.

In comparison, a pentasupertetrahedral cluster is considerably larger than a supertetrahedral cluster of the same order. The formulas for discrete Tn clusters are: T1 (MX_4), T2 (M_4X_{10}), T3 ($M_{10}X_{20}$), T4 ($M_{20}X_{35}$) and so on. The Pn cluster is composed of four same order Tn clusters at the corner and one anti-Tn cluster at the core. For example: the P1 cluster consists four T1 clusters (MX_4) and one anti-T1 (XM_4) cluster at the center, resulting in the composition $((MX_4)_4(XM_4)$ (i.e. M_8X_{17}). The supertetrahedral clusters as large as T5 are known [9], but the largest known cluster of the P*n* series is the P2 cluster [8].

In this study, we employ 4,4′-trimethylene dipiperidine (TMDP), and histidine as the structure-directing agents for the synthesis of compound with mixed supertetrahedral chalcogenide clusters T2, (Fig. 1(a)), and pentasupertetrahedral chalcogenide clusters P1, (Fig. 1(b)). The TMDP is widely used as a structure construction template in the synthesis of T*n* series chalcogenide clusters [10]. The use of amino acid in the hydrothermal synthesis for an inorganic tetrahedral cluster has not been reported. In this case, we find that the porosity of the mixed chalcogenide clusters with a TMDP only template is about 5.5% smaller than the one with TMDP and histidine as templates. On the basis of experimental data, the role of histidine in the formation of mixed chalcogenide clusters is to improve the pore size of the 2-D frame work, and the porosity of the crystal.

A typical synthesis of reddish crystal $[In_{12}S_{21}(Se_3)H_2]^{10-}$ clusters, denoted as NCYU-5, was prepared by the reaction of indium powder (60 mg, 99.99%, Aldrich), sulfur powder (92 mg, 99.95%, Aldrich), selenium powder (17 mg, 99.5%, Showa), and a solution mixture of H_2O (1.95 mL), NaOH (1 M, 0.1 mL), histidine (0.26 g, 98%, Fluka) and TMDP (97%, 0.25 g, Aldrich) in a 30 mL Teflon-lined stainless steel autoclave. The reactants were stirred for 30 min before the sealed vessel was heated at 150 °C for 3 days. After the reaction had finished, the autoclave was allowed to cool down to room temperature in atmosphere for several hours. The weight ratio between Se/S should be carried out very precisely. If the derivation of the Se/S weight ratio

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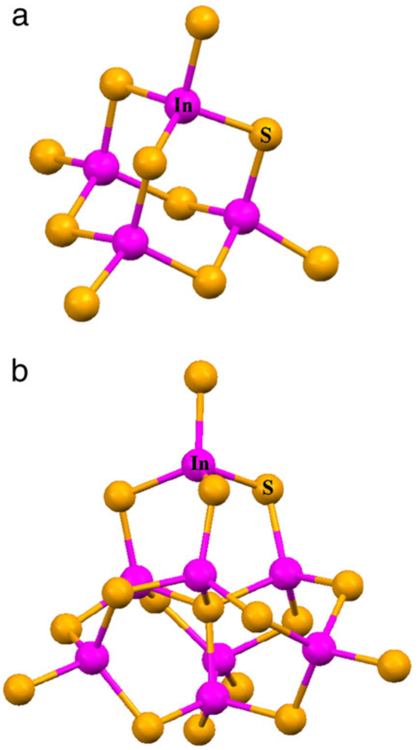

Fig. 1. Diagram of (a)T2 cluster (In_4S_{10}), (b) P1 cluster ($(InS_4)_4(SIn_4)$ (i.e. In_8S_{17}).

Table 1
Summary of ICP-MS data of S and Se concentration in NCYU-5.

Wavelength	S = 180.676 nm		Se = 196.026 nm	
Sample name	Cc(ppb)	RSD(%)	Cc(ppb)	RSD(%)
1	779	4.2	103	2.3
2	832	3.7	126	2.9
3	835	0.9	125	1.8
4	837	0.9	117	1.5
4	887	2.9	156	0.8

is more than ±3%, no crystal could be found in the final product. The product was washed several times by a mixture of ethanol and methanol to remove any residue on crystals. The crystals are stable in air, water, or polar solvents for more than three months. The yield of NCYU-5 is generally above 55% in weight.

Table 2
Summary of Crystal Data and Refinement for NCYU-5.

Name	NCYU-5
Empirical formula	$In_{12}S_{22}Se_3H_2$
Temperature	293(2) K
Crystal size (mm3)	0.08 × 0.07 × 0.07
Crystal system	Trigonal
Space group	P 3 1 c
Unit cell	a = 16.5064(15) Å c = 25.018(3) Å
Volume	5903.2(10) Å^3
Z	6
Reflections collected	67,260
Independent reflections	9756 [R(int) = 0.0972]
Final R indices [I > 2sigma(I)]	R1 = 0.0527, wR2 = 0.1125
R indices (all data)	R1 = 0.0900, wR2 = 0.1228
Goodness-of-fit on F^2	0.878

The geometry of indium chalcogenide $[In_{12}S_{21}(Se)_3H_2]$ crystal is hexagonal. The scanning electron microscopy (SEM) image is given in the supporting information. Crystallographic structures of NCYU-5 were solved from single crystal X-ray diffraction. Data were collected at room temperature on a SMART CCD diffractometer with Mo-Kα radiation. All framework atoms can be determined and the guest molecules are disordered inside the large cavities. One of the most interesting features in NCYU-5 is that the compound has two different types of clusters: pentasupertetrahedral P1 cluster, and adamantine-shaped T2 cluster. The chemical formula for discrete P1 and T2 is $[In_8S_{17}]^{10-}$ and $[In_4S_{10}]^{8-}$, respectively.

In the T2 cluster, nine sulfur sites are coordinated to two indium sites. As for the four corner sulfur sites, one corner sulfur site is terminated as an —SH group, and the other three are shared between adjacent P2 clusters. The purpose of the assignment of H atom is to balance the charge of the chemical formula. Although, the H atoms are not able to be solved in the refinement of crystal structure, the protonation of an S atom will affect the In—S bond length, and bond valence. The variations of bond length and bond valence of the corner S atom offer the evidence of protonation. Such as in the T2 cluster, the bond length of In_1—S_1 (2.517 Å) is longer that of In_1—S_2 (2.505 Å). The bond valence of S_1(0.672) shows a smaller value, in comparison with S_2(0.694). It is reasonable to assign an H atom to the corner S(1), and the corner sulfur site is terminated as an —SH group. Therefore, the T2 cluster in the framework is written as $[In_4S_6(S_3)_{1/2}SH]^{8-}$. For the same reason, the P1 cluster is written as $[In_8S_{13}\ (S_3)_{1/2}\ SH]^{6-}$.

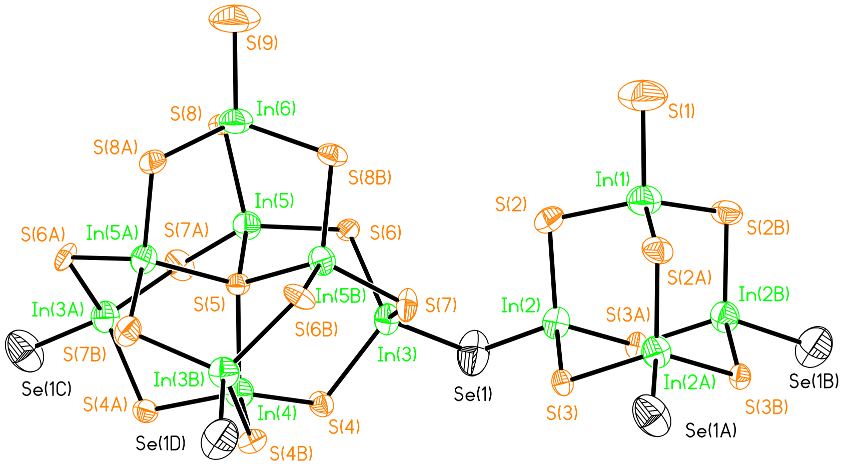

Fig. 2. An illustrated unit cell structure for NCYU-5. The calculated occupancy possibility of the Se(1) site for Se to S is ~90%. The occupancy possibility of the S3 site in the T2 cluster for Se to S is ~10%. The temperature factor plays an important role in the refinement of S and Se locations.