Inorganic Chemistry
Communication

Indium−Sulfur Supertetrahedral Clusters Integrated with a Metal Complex of 1,10-Phenanthroline

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A new type of indium−sulfur supertetrahedral compound with unique optical absorption property has been synthesized and characterized crystallographically, in which discrete or polymeric InS-T3 clusters are integrated with metal complex cations of 1,10-phenanthroline.

The most common chalcogenide clusters of indium and gallium are a series of supertetrahedral clusters denoted as Tn ($n = 2-5$, number of metal layers). Substantial success on these types of clusters has been achieved[1] because they can serve as building blocks for constructing crystalline porous frameworks[2] with semiconductive properties.[3] To further promote the potential applications of chalcogenidometalates in photoelectronic materials, it is highly desirable to develop hybrid materials that allow uniform molecular-level integration of crystalline semiconducting frameworks with optically active guest species.[4]

The metal (M) complexes of 1,10-phenanthroline (phen) have been interesting until now for their application in photoelectronic materials. The Ru^{II}phen system offers extensive applications in solar light harvesting and energy conversion.[5] Besides the Ru^{II}phen complexes, Cu^{I}phen,[6] Fe^{II}phen,[7] and so on are also candidates for photochemical sensitizers. However, most M-phen complex sensitized inorganic semiconductors are surface-modified or embedded multicomponent materials.[5d] The fundamental study devoted to the single-phase semiconducting materials cocrystallized with M-phen complex cations is particularly challenging.

Despite extensive research on supertetrahedral clusters of metal chalcogenide, little is known about related chalcogenidometalates integrated with metal complexes of phen. Most known compounds are charge and space compensated by various amines.[1−3] Because of the higher energy gap of these semiconductive chalcogenidometalates, the available absorption bands were mainly located at the violet or near-violet region. The only example that demonstrates the use of [M(1,10-phen)$_3$]$^{2+}$ as templates to organize tetrahedral chalcogenido clusters into unique crystals was reported by Feng's group four yeas ago.[4] The anion of these compounds is a thiophenol-capped T4 cluster, [Cd$_{32}$S$_{14}$(Sph)$_{40}$]$^{4−}$. The non-capped tetrahedral cluster with the complex of M-phen has not been reported yet based on our knowledge. We report herein the first example of InS-T3 clusters with cocrystallized Ni-phen complex cations: Mp-InS-**1**, Mp-InS-**2**, and Mp-InS-**3**. Structural and optical characteristics of these compounds are discussed.[8]

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(8) X-ray crystallography. **1**, monoclinic, $P2_1/a$, $a = 24.255(2)$ Å, $b = 20.824(2)$ Å, $c = 27.881(2)$ Å, $\beta = 103.137(3)°$, $M_r = 3843.5$, $S = 1.043$, $R_{gt} = 0.0747$, wR = 0.1685. **2**, triclinic, $P\bar{1}$, $a = 16.262(1)$ Å, $b = 18.262(1)$ Å, $c = 26.259(2)$ Å, $\alpha = 80.874(5)°$, $\beta = 82.913(5)°$, $\gamma = 64.515(3)°$, $M_r = 7639.01$, $S = 1.015$, $R_{gt} = 0.0707$, wR = 0.1342. **3**, triclinic, $P\bar{1}$, $a = 11.872(1)$ Å, $b = 16.198(2)$ Å, $c = 29.0471(3)$ Å, $\alpha = 81.602(3)°$, $\beta = 86.877(4)°$, $\gamma = 80.291(3)°$, $M_r = 2992.4$, $S = 1.095$, $R_{gt} = 0.0932$, wR = 0.1787.
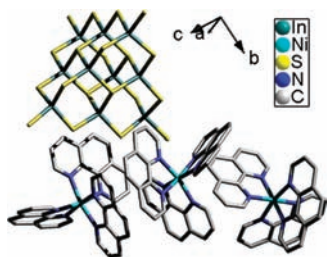
Figure 1. Structure of compound Mp-InS-**1**. HDMA and water molecules were omitted for clarity.

The fundamental structure of Mp-InS-**1** (Figure 1) consists of a discrete T3 cluster of $[H_nIn_{10}S_{20}]^{(10-n)-}$ with three $[Ni(phen)_3]^{2+}$. The crystal belongs to a $P2_1/a$ space group with four formulas in one crystal unit. The indium atoms are tetrahedrally coordinated by sulfur atoms that exhibit terminal and bi- and tribridging modes. The average distances of the In−S bonds are 2.431 Å for the bibridging mode and 2.511 Å for the tribridging mode and are on the order of bibridging < tribridging mode in accordance with those reported.[2,3] The terminal In−S distances are 2.462(3), 2.476(3), 2.495(3), and 2.491(3) Å for In(1)−S(1), In(10)−S(20), In(7)−S(17), and In(5)−S(11), respectively. Although the protons are unable to be observed directly from the Fourier map, the longer terminal In−S distances of S(17) and S(11) imply that the terminal sulfur atoms are likely to be protonated.[9] For example, in the structure of $[C_6H_{16}N]_4In_4S_{10}H_4$,[9a] the average length of the terminal In−S bonds is longer than that of the bridging ones, suggesting the presence of terminal −SH groups for the isolated In_4S_{10} anions. Therefore, deduced from the results of X-ray structure analysis, elemental analysis, the principle of charge balance, and IR spectra (SI-Fig.-1 in the Supporting Information), in Mp-InS-**1**, there are seven water molecules and two protonated DMA molecules (DMA = dimethylamine), which are byproducts of a N,N-dimethylformamide (DMF) solvothermal system.[10] The accurate formula of Mp-InS-**1** should be $\{[Ni(phen)_3]_3 \cdot H_2In_{10}S_{20}\} \cdot 2HDMA \cdot 7H_2O$. The fundamental structure of Mp-InS-**2** is similar to that of Mp-InS-**1**, while the crystal belongs to a $P\bar{1}$ space group with two formulas in one crystal unit. The average distances of the In−S bonds are 2.430 Å for the bibridging mode and 2.505 Å for the tribridging mode. The terminal In−S distances of Mp-InS-**2** are 2.489(2), 2.484(3), 2.474(3), and 2.482(2) Å for In(1)−S(1), In(4)−S(8), In(6)−S(11), and In(10)−S(20), respectively. The distances also indicate that the terminal sulfur atoms might be protonated. The formula of Mp-InS-**2** should be $\{[Ni(phen)_3]_3 \cdot H_4In_{10}S_{20}\} \cdot 14.5H_2O$.

The T3 clusters in Mp-InS-**1** and Mp-InS-**2** are distributed in a layered arrangement parallel to the *ab* plane and sandwiched within two layers of $[Ni(phen)_3]^{2+}$ cations (Figure 2). In the layer, the clusters are alternately arranged in an up and down fashion, ensuring that one of the tetrahedral faces of the T3 cluster is on the surface of the layer. Some cations are embedded in the T3 cluster layer to separate the clusters and avoid formation of a polymeric structure. Therefore, the $[Ni(phen)_3]^{2+}$ cation serves as an aromatic environment to stabilize the isolated $[H_nIn_{10}S_{20}]^{(10-n)-}$ T3 clusters. There are
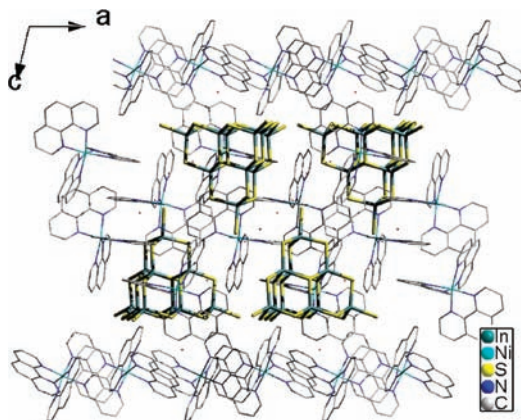

Figure 2. Molecular packing of Mp-InS-**1** showing the layered structure (viewed along the *b* direction).

two types of important intermolecular interactions: S···C contacts between cations and anions and C···C stacking of the phen planes. The S···C contacts range from 3.389 to 3.485 Å for Mp-InS-**1** and from 3.295 to 3.492 Å for Mp-InS-**2**. The average distances of C···C stacking are 3.368 and 3.316 Å for Mp-InS-**1** and Mp-InS-**2**, respectively (SI-Table 1 in the Supporting Information). These interactions involve $\pi \cdots \pi$ and p$\cdots \pi$ overlaps that overcast the whole crystal lattice, which might be an important structural characteristic for these inorganic−organic hybrid materials.

The Tn ($n = 2-5$) clusters of In^{III}/Ga^{III} have been found to be useful building blocks for the construction of covalent superlattices. Through sharing of the corner chalcogen atoms, these clusters usually form a polymeric framework, especially 3D porous structures.[1−3] On the other hand, a lot of isolated T2 clusters of $[Ge^{IV}_4Q_{10}]^{4-}$ have been prepared.[11] Isolated T3 clusters of Cd/ZnSph and Cd/ZnSeph, in which the surface is capped by thiophenol, and T3 clusters terminated by metal amine complexes are also well-known.[12,13] Inconceivably, limited discrete noncapped Tn ($n > 3$) clusters have been reported until now, though this system has been extensively studied. The only example of a discrete supertetrahedral cluster is a T2 × T4 In−S cluster,[1e] in which the nonprotonated terminal In−S bond length is 2.415 Å, much shorter than those of the bridging bonds. Compounds Mp-InS-**1** and Mp-InS-**2** reported in this work contain unusual isolated noncapped T3 clusters. The stability of these isolated T3 clusters is ascribed to the steric hindrance of the cations $[Ni(phen)_3]^{2+}$ and the global charge balance of the cations and anions along with the interactions between them. However, the powdered crystals are sensitive to air.

Compounds Mp-InS-**1** and Mp-InS-**2** successfully combine the tetrahedral T3 cluster with the M-phen cation, which is a new achievement in crystal engineering. The discrete clusters might have a potential application as precursors for

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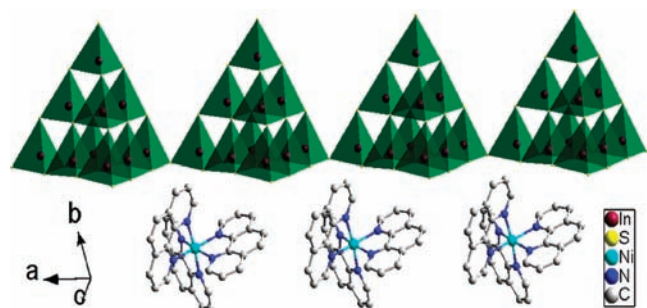
Figure 3. 1D polymeric structure of Mp-InS-**3**. Each $[In_{10}S_{20}]^{n-}$ cluster is represented by a supertetrahedron with 10 InS$_4$ tetrahedra.
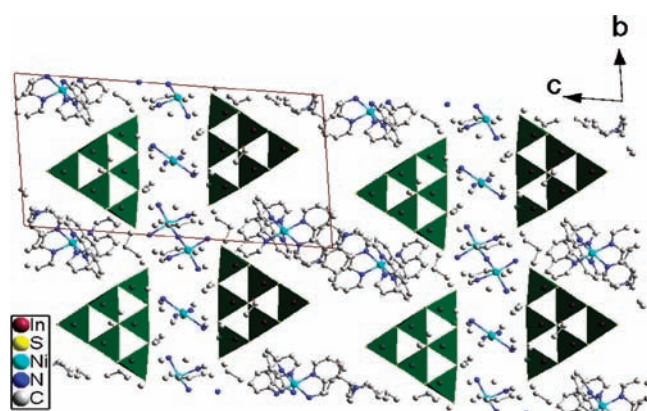

Figure 4. Molecular packing of Mp-InS-**3** (viewed along the *a* direction, the axis of the T3 cluster chains).

further assembly, but compounds **1** and **2** are insoluble in common solvents and even have very low solubility in DMF. The aim of our research is the single-phase dye-sensitized semiconductor, in which polymeric chalcogenidometalates cocrystallized or coordinated with M-phen complexes have the most potential as candidates. Because of the large size and rigid structure of the complex of M-phen, there seems to be more effort needed to achieve that goal. On the basis of our experiences in the syntheses of Mp-InS-**1** and **2**, in which the semiconductive structures are discontinuous, a polymeric compound Mp-InS-**3** has been obtained, in which M-phen complex cations are integrated with T3 cluster chains. The 1D structure is assembled by $[In_{10}S_{20}]^{n-}$ clusters sharing two of the terminal sulfur atoms (Figure 3). The crystal of Mp-InS-**3** is triclinic and belongs to a $P\bar{1}$ space group. The terminal In−S distances of the T3 cluster in Mp-InS-**3** separate into two groups. The shorter ones are the bridging In(6)−S(11) and In(5)−S(11) bonds, 2.463(3) and 2.461(3) Å, respectively, and the longer ones are the protonated terminal In(1)−S(1) and In(10)−S(19) bonds, 2.497(4) and 2.481(4) Å, respectively. Thus the formula of Mp-InS-**3** should be $\{[Ni(phen)_3]_3\cdot H_2In_{10}S_{19}\}_n$. Parts of the cations are unable to be mapped for their mobility in the lattice space. Figure 4 shows the molecular packing of the anions. Two T3 cluster chains pass through the crystal cell along the *a* direction, and the undersides of the T3 clusters are in a face-to-face fashion. The complex cations surround the chains filling the space.

UV−vis absorption spectra of indium sulfides were calculated from the data of diffuse reflectance and are depicted in Figure 5 and SI-Fig.-2 in the Supporting Information. The spectra of Mp-InS-**1** and Mp-InS-**2** are similar and can be
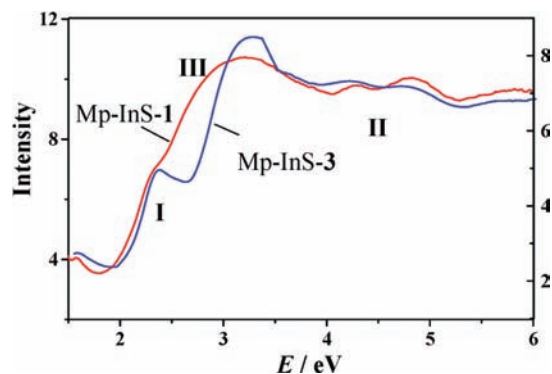

Figure 5. Electronic spectra of Mp-InS-**1** (red line) and Mp-InS-**3** (blue line) in the solid state at room temperature.

assigned to two main parts, bands I and II. The first set of bands (band I), about 2.36 eV, in the visible area is assigned to the d−d transition of the $[Ni(phen)_3]^{2+}$ cations (see SI-Fig.-3 in the Supporting Information, the spectrum of $[Ni(phen)_3]Cl_2$). The second set of bands (band II) is in the area above about 3.2 eV. These intense bands are assigned to cluster-centered bands, with overlapped ligand-centered bands typically the $\pi\cdots\pi^*$ transitions of the phen ligand. When the spectrum of Mp-InS-**1** (or **2**) is compared with that of Mp-InS-**3**, a shoulder peak (band III located around 2.8 eV) can be observed clearly for the former, which reflects the charge transfer (CT) between cations and anions due to the strong $p\cdots\pi$ overlaps (S$\cdots$C contacts; SI-Table 1 in the Supporting Information). The dark red color of the compounds Mp-InS-**1** and Mp-InS-**2** also supports the fact that there is intense CT between cations and anions because the color of $[Ni(phen)_3]^{2+}$ is pink and $[In_xS_y]^{n-}$ should be colorless. Though In^{III} is an electron-poor center, the cluster is an electron-rich donor owing to the sulfur atoms and the electron-delocalized state within the cluster. The CT band is an important characteristic for a metal complex sensitized semiconductor. Because the interaction between cations and anions in Mp-InS-**3** is comparatively weak, with part of the complex cations being seriously disordered, the CT band of **3** is not as notable as those of **1** and **2**.

In summary, a new type of T3 supertetrahedral compound has been synthesized. Compounds Mp-InS-**1** and Mp-InS-**2** are discrete $[H_nIn_{10}S_{20}]^{(10-n)-}$ clusters with protonated terminal sulfur atoms. The cluster anions are integrated with complex cations of $[Ni(phen)_3]^{2+}$, forming a single-phase material having intense CT between cations and anions. The unusual stability of the isolated T3 clusters and the unique spectra were ascribed to the strong S$\cdots$C contacts between cations and anions. Compound Mp-InS-**3** is a novel 1D polymeric structure integrated with metal complex cations of phen. Unfortunately, the interaction between cations and anions is not very strong for the unfitted space filling. Anyway, the research on dye- or complex-sensitized inorganic−organic hybrid single-phase compounds for photophysical applications is an attractive challenge that we faced.