Inorganic Chemistry
Communication
pubs.acs.org/IC

Synthesis, Crystal Structure, and Optical Properties of a Three-Dimensional Quaternary Hg−In−S−Cl Chalcohalide: $Hg_7InS_6Cl_5$

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Supporting Information

ABSTRACT: A crystalline three-dimensional (3D) quaternary chalcohalide, $Hg_7InS_6Cl_5$ (**1**), has been synthesized through a solid-state reaction under medium temperature. It is the first example in the family of the Hg−IIIA−Q−X (Q = S, Se, Te; X = F, Cl, Br, I) systems. Compound **1** features a 3D network and has an optical band gap of 2.54 eV.

Metal chalcohalides, coming from the combination of chalcogenides and halides, are of special interest because these materials not only have diverse structural chemistry and tunable electronic properties but also have practical applications in nonlinear optics, upconversions, phase-transitions, X-ray detection, and so on.[1−4] More interestingly, single chalcohalide compound with two (or more) different metal ions could provide much richer structural features and more chances to tune their bandgaps. However, it is more challenging to prepare such complexes due to the greater possibility to form binary and ternary complexes. This problem could be solved if a larger metal center with a flexible coordination environment had been selected.

In our research, we are interested in mercury(II)-related chalcohalides not only because mercury ions usually adopt the closed-shell $[Xe]4f^{12}5d^{10}$ electronic configuration, have a larger radius, and possess the diverse coordination geometry varying from linear to octahedral but also because the mercury(II) ion has a greater tendency to form all kinds of architectures covering 0D, 1D, 2D, and 3D topologies.[5] In addition, mercury(II)-based materials have several applications in the fields of catalysts, nonlinear optics, infrared detection, and so forth.[6,7]

Solid state reaction and hydro(solvo)thermal methods[8,9] as two basic standard synthesis techniques have been proved to be powerful tools to explore a variety of mercury complexes.[10,11] A number of inorganic supramolecular compounds containing mercury, constituting an important subset of mercury complexes, have been synthesized through solid state reaction, and physical and chemical properties have also been well studied. In most cases, mercury-based supramolecular compounds have positive host fragments and negative guest species.[12,13] Another important branch of mercury complexes is the quaternary Hg−M−Q−X systems (M = p-block or d-block elements; Q = S, Se, Te; X = F, Cl, Br, I), in which M is focused largely on IB, IIB, IVB, IVA, and VA elements.[10,14−16] However, to the best of our knowledge, no quaternary Hg−IIIA−Q−X compound has been reported so far. We report here a quaternary compound, $Hg_7InS_6Cl_5$ (**1**), which exhibits a novel 3D network and is the first example of a quaternary phase in the Hg−IIIA−Q−X systems.

In a typical synthesis, compound **1** was prepared through solid state reaction from a mixture containing Hg_2Cl_2 (0.875 mmol; *note: great attention should be paid due to the toxicity of mercury and extreme care must be taken when handling sample and products*), In_2S_3 (0.25 mmol), and S (2.25 mmol), which were loaded and sealed in an evacuated fused silica tube (12 mm i.d.) under high vacuum conditions ($\sim 10^{-3}$ Pa). The sealed tube was vertically placed in a furnace and heated at 450 °C for 4 days and then slowly cooled to room temperature. The light yellow block-shaped products were sublimed and crystallized on the top part of tube wall, while the other phases (most are binary and ternary phase) stayed at the bottom of the tube. It is easy to collect the target compound. The purity of the sample was confirmed by X-ray diffraction (XRD) patterns (Figure S1), and it is stable in the air at room temperature. The calculated atomic Hg/In/S/Cl ratio from the single-crystal structure analysis is in suitable agreement with energy-dispersive X-ray spectroscopy (EDS) analysis (Figure S2).

The single crystal data were collected on a Bruker APEX II CCD diffractometer at 293 K. The X-ray crystallography study reveals that compound **1** crystallizes in a new structure type with the triclinic space group $P\bar{1}$ (No. 2).[17] The structure features a novel 3D network, containing 2D Hg/In/S layers which are bridged by mercury atoms (Figure 1). The asymmetric unit of **1** contains 20 crystallographically unique sites: one In site, eight Hg sites, six S sites, and five Cl sites (Figure 1a). Interestingly, the In(1) site adopts distorted octahedral coordination with two S atoms and four Cl atoms (Figure S3). The In−S bond distances are 2.591(2) and 2.672(2) Å, and the In−Cl bond distances vary from 2.479(3) to 2.560(2) Å, which are comparable to those in $InSb_2S_4Cl$ and In_5S_5Cl.[18] Although there are eight Hg sites in the unit, three types of coordination geometries are formed: Hg(2) and Hg(4) display a Y shape, Hg(3) and Hg(6) exhibit a nearly T shape, and the others show a linear shape (Figure S3). The Hg−Cl bond lengths are 2.820(3) and 2.905(2) Å, and the Hg−S bond distances fall in the range of 2.349(2)−2.688(2) Å, which agree with those in CuHgSCl, Hg_3AsS_4Cl, and $Hg_3ZnS_2Cl_4$.[10b,13b,16c] All S atoms acting as tridentate metal linkers are trigonally coordinated by In and Hg atoms. S(1) and S(2) bridge to one

Received: December 22, 2011
Published: March 29, 2012

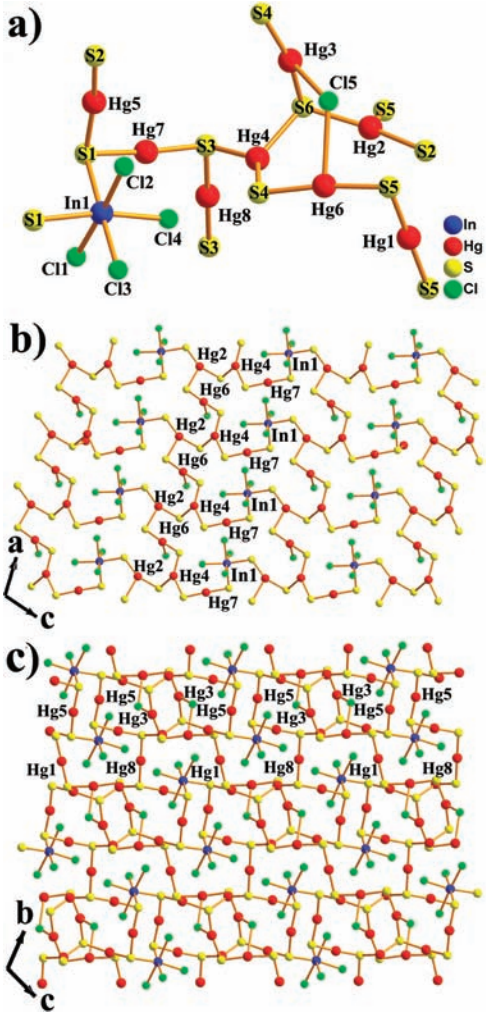

Figure 1. (a) Ball-and-stick model of the relevant fragments of compound **1** with atomic labels. (b) View of a single Hg/In/S layer of compound **1** along the *b* direction. (c) Projection of the three-dimensional network of **1** along the *a* direction.

In atom and two Hg atoms, respectively, whereas the other S atoms are coordinated with three Hg atoms. All Cl atoms coordinated with the In(1) atom are unidentate terminal ligands, while Cl(5) serves as a bidentate metal linker which is coordinated by two Hg atoms.

In the structure, trigonal coordinated Hg(2), Hg(4), and Hg(6) and linear coordinated Hg(7), via sharing S atoms to form a 1D branch polymer, the side branches of which are made of S, Cl, and Hg(7)S_2, approximately parallel the *a* direction (Figure 1b). Meanwhile, the 1D branch polymer is interconnected by distorted octahedral In(1)S_2Cl_4 via vertex-sharing S atoms to form a 2D layer parallel to the *ac* plane (Figure 1b). Along the *b* axis, two neighboring layers are further bridged by the Hg(3) and Hg(5) linkers to generate the condensed bilayer substructure. And then, these 2D substructures are laid to overlap each other via the Hg(1) and Hg(8) linkers to construct the overall 3D network (Figure 1c).

The solid state UV−visible absorption for compound **1** has been measured by the diffuse-reflectance spectra at room temperature, as shown in Figure 2. It reveals the presence of an optical absorption edge in the visible region and the optical band gap at 2.54 eV. Such an energy gap falls in the range of a semiconductor and is consistent with the yellow color of the crystals. The band gap is smaller than that of binary Hg_2Cl_2 (3.2 eV)[19a] and ternary $CsInS_2$ (2.0 eV);[19b] larger than those of binary α-HgS (2.1 eV),[19c] β-In_2S_3 (2.0−2.3 eV),[19d] quaternary $CaYbInS_4$ (3.4 eV),[19e] and $AuPb_8In_{17}S_{34}$ (1.3 eV);[19f] and comparable to that of quaternary $Hg_3ZnS_2Cl_4$ (2.71 eV)[16c] and the theoretical band gap of $HgCl_2$ (2.49 eV).[19g] It is worth noting that the band gap of **1** falls in between those of starting materials Hg_2Cl_2 (3.2 eV) and β-In_2S_3 (2.0−2.3 eV). This result might offer us a possible way to tune the band gaps of known materials through halide doping.

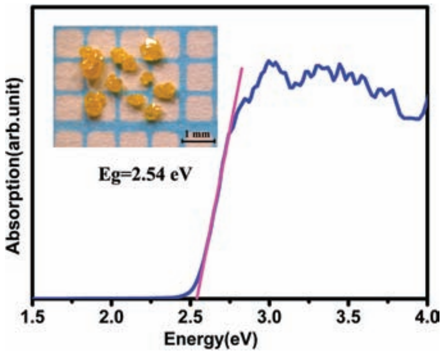

Figure 2. UV−visible absorbance of compound **1**. Insert is the picture of as-prepared crystals.

In summary, a quaternary chalcohalide, $Hg_7InS_6Cl_5$ (**1**), has been successfully synthesized through solid-state reaction at a medium temperature (450 °C). X-ray single crystal diffraction analysis shows that there is one In and eight Hg unique sites in the unit cell, which are bridged by S and Cl atoms to construct a complicated 3D network. Solid-state optical properties of as-prepared compound (**1**) indicate that it is a wide bandgap semiconductor with an optical band gap of around 2.54 eV. Complex **1** is the first example in the family of the quaternary Hg−IIIA−Q−X system, and appropriate chemical substitution in this system may be worth exploring to enrich chalcohalides.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF data, experimental methods, and additional tables and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Q.Z. is thankful for the support from the NTU start-up grant and Tier 1 fund from MOE. This research is supported by the Singapore National Research Foundation under CREATE programme: Nanomaterials for Energy and Water Management, and Singapore MPA 23/04.15.03 RDP 009/10/102 grant.

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(17) Crystallographic data for **1**: $Hg_7InS_6Cl_5$, $M_r = 1888.62$, triclinic, space group $P\bar{1}$ (No. 2), $a = 7.3743(5)$ Å, $b = 10.4520(8)$ Å, $c = 13.7521(11)$ Å, $\alpha = 109.415(3)°$, $\beta = 105.264(3)°$, $\gamma = 93.746(3)°$, $V = 950.71(12)$ Å^3, $Z = 2$, $\rho_{\text{caled}} = 6.597$ gcm^{-3}, $F(000) = 1579$, GOF = 1.120. A total of 12 234 reflections were collected, 3354 of which were unique ($R_{\text{int}} = 0.0401$). $R_1 = 0.0268$ and $wR_2 = 0.0554$ for all data, $R_1 = 0.0236$ and $wR_2 = 0.0507$ for data with $I > 2\sigma(I)$.

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