

Two Gallium Antimony Sulfides Built on a Novel Heterometallic Cluster

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Two gallium antimony sulfides, $[\text{Ni}(\text{en})_3][\text{Ga}_2\text{Sb}_2\text{S}_7]$ (**1**) and $[(\text{Me})_2\text{NH}_2]_2[\text{Ga}_2\text{Sb}_2\text{S}_7]$ (**2**), have been prepared under mild solvothermal conditions. Both structures feature a two-dimensional network in which two GaS_4 tetrahedra and two SbS_3 trigonal pyramids are combined to form a heterometallic cluster of $\{\text{Ga}_2\text{Sb}_2\text{S}_9\}$ as a new secondary building unit. The thermal properties of **1** and **2** have been studied by thermogravimetric analysis, and the optical properties of **1** and **2** have been characterized by UV–vis spectra.

The current increasing interest in metal chalcogenides stems not only from their fascinating architectures and topologies but also from their potential applications in areas such as fast-ion conductivity, photocatalysis, electrooptics, sensors, and thermoelectrics.¹ An effective strategy for the development of metal chalcogenides is to rationally design and construct new secondary building units (SBUs). In the metal chalcogenide family, substantial works have been reported on those based on the supertetrahedral clusters (*Tn*, *Pn*, *Cn*) with tunable components and sizes as SBUs, which are constructed from the fundamental building units with the same geometry, namely, metal chalcogenide tetrahedra of groups 13 (Ga and In) and 14 (Ge and Sn) and some transition-metal (TM) elements.^{1a–d,2} On the other hand, the M^{3+} ($\text{M} = \text{As}, \text{Sb}$) cations of group 15 tend to adopt asymmetric coordination geometry such as the pyramidal MQ_3^{3-} ($\text{M} = \text{As}, \text{Sb}; \text{Q} = \text{S}, \text{Se}, \text{Te}$) units, which

give rise to another type of SBUs such as a $[\text{Sb}_3\text{S}_6]^{3-}$ semicube.³ Despite many SBUs reported, relatively little progress has been made on metal chalcogenides built on SBUs integrating both tetrahedra and other polyhedra, in particular those possessing asymmetric coordination. For group 15 metal chalcogenides, some thio- and selenoarsenates combining metal ions (In^{3+} , Hg^{2+} , Ag^+ , etc.) have been reported.⁴ Metal chalcogenides based on the combination of TM tetrahedra and asymmetric coordination polyhedra of Sb^{III} have been also isolated,⁵ whereas those containing both main-group metal tetrahedra and asymmetric coordination polyhedra of Sb^{III} are less explored.⁶ For group 13 metal chalcogenides, although lots of indium chalcogenides have been reported,^{1a–d,2a,d,e} only a few gallium chalcogenides have been described.^{1b,2a,b,f,7} Recently, indium antimony sulfide containing InS_4 tetrahedra and SbS_3 trigonal pyramids has been synthesized.⁸ However, chalcogenides incorporating tetrahedra of Ga^{III} and asymmetric coordination polyhedra of Sb^{III} have not been to date documented.

Our recent research is focused on exploring new SBUs for metal chalcogenides by integrating main-group metal tetrahedra with group 15 metal asymmetric coordination polyhedra, such as $\text{Sb}^{\text{III}}\text{Q}_n^{x-}$ ($\text{Q} = \text{S}, \text{Se}; n = 3, 4; x = 3, 5$), in the presence of various organic amines or $[\text{TM}(\text{amine})_m]^{n+}$

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complexes as the templates or structure-directing agents. Studies indicate that the asymmetric coordination geometry adopted by the ions (such as Se^{4+} , Te^{4+} , and Sb^{3+}) with stereochemically active lone-pair electrons can induce non-centrosymmetric structures, which might engender interesting physical properties such as second-harmonic generation.⁹ We deem that such an approach would lead to the formation of various heterometallic SBUs, further generating novel open-framework chalcogenides with diverse architectures and properties. Indeed, it has been confirmed by the successful isolation of the first three-dimensional (3D) chiral microporous germanium antimony sulfide with excellent ion-exchange properties reported by us, namely, $[(\text{Me})_2\text{NH}_2]_2\text{-}[\text{Sb}_2\text{GeS}_6]$, which combines GeS_4 tetrahedra and $\Psi\text{-SbS}_4$ trigonal bipyramids into one single structure.¹⁰ As the continuity and development of our research, herein we report two gallium antimony sulfides, namely, $[\text{Ni}(\text{en})_3][\text{Ga}_2\text{Sb}_2\text{S}_7]$ (**1**; en = ethylenediamine) and $[(\text{Me})_2\text{NH}_2]_2[\text{Ga}_2\text{Sb}_2\text{S}_7]$ (**2**).

Compound **1** was prepared from a mixture of Ga, Sb, S, and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in ethylenediamine, which was sealed in a stainless steel reactor with a 28 mL Teflon liner, heated at 190 °C for 7 days. The product consisted of many yellow lathe crystals of **1** and a few violet blocklike crystals, together with a small amount of indefinite yellow powder. The violet blocklike crystals were identified by single-crystal X-ray diffraction as $[\text{Ni}(\text{en})_3]\text{Ga}_2\text{S}_4$, which has been reported.^{7b} During the synthesis, $[\text{Ni}(\text{en})_3]^{2+}$ as template cations were in situ formed, which has been found in many chalcogenides.¹¹ Compound **2** was solvothermally prepared in a similar procedure. A mixture of Ga, Sb, S, and triethylenediamine in *N,N'*-dimethylformamide (DMF) was heated at 190 °C for 14 days to yield the yellow lathe crystals of **2**, together with a small amount of indefinite yellow powder. In the preparation of **2**, DMF served as the solvent and underwent hydrolysis to produce dimethylammonium as cations entering the structure.¹⁰

1 and **2** represent two organically templated gallium antimony sulfides. Their structures are similar and feature an inorganic anionic two-dimensional (2D) network built upon the novel Ga/Sb heterometallic cluster as a SBU with the template cations located at the interlayer space. The asymmetric unit of **1** contains two crystallographically independent Ga^{3+} ions, two Sb^{3+} ions, seven S^{2-} ions, and one $[\text{Ni}(\text{en})_3]^{2+}$ cation, respectively (Figure S1 in the Supporting Information). Both Ga^{3+} ions are tetrahedrally surrounded by four S^{2-} ions. Both Sb^{3+} ions adopt a SbS_3 trigonal-pyramidal coordination geometry, with $\text{Sb}^{\text{III}}\text{-S}$ bond lengths ranging from 2.415(2) to 2.467(2) Å. Each S^{2-} anion acts as a bidentate metal linker. Two GaS_4 tetrahedra and two SbS_3 trigonal pyramids are interconnected by corner-sharing to form a novel tetranuclear heterometallic cluster

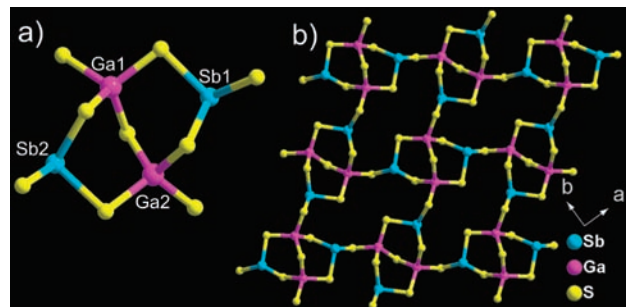


Figure 1. (a) Novel tetranuclear heterometallic cluster of $\{\text{Ga}_2\text{Sb}_2\text{S}_9\}$. (b) 2D anionic network of $[\text{Ga}_2\text{Sb}_2\text{S}_7]^{2-}$ along the *ab* plane.

with a stoichiometry of $\{\text{Ga}_2\text{Sb}_2\text{S}_9\}$ as the SBU (Figure 1a), in which there exist two Ga_2SbS_3 rings. Although similar building units of $[\text{Ga}_4\text{Q}_7(\text{en})_2]^{2-}$ ($\text{Q} = \text{S}, \text{Se}$) have been reported from the view of the shape,^{7a,b} they are composed of tetrahedra of Ga^{III} only, whereas $\{\text{Ga}_2\text{Sb}_2\text{S}_9\}$ is a new SBU comprising tetrahedra of Ga^{III} and asymmetric coordination polyhedra of Sb^{III} .

It is worth noting that the pyramidal MQ_3^{3-} ($\text{M} = \text{As}, \text{Sb}; \text{Q} = \text{S}, \text{Se}$) anions often undergo a variety of self-condensation to form polyanion units such as oligomeric chains or rings as SBUs and then connect with other metal ions to form heterometallic chalcogenides.^{4,5} Occasionally, the MQ_3^{3-} anion itself can act as part of an anionic structure,^{4c,5c} but no obvious heterometallic SBU is found. In the group 15/16 chalcogenides, SBUs such as $[\text{In}_5\text{Sb}_6\text{S}_{19}]^{5-}$ with two identical bicyclic subfragments have been isolated.⁸ However, SBUs with different components and various architectures are still limited. It is undoubted that the current tetranuclear heterometallic cluster of $\{\text{Ga}_2\text{Sb}_2\text{S}_9\}$ endues a new SBU of chalcogenides, realizing the novel $\text{Ga}^{3+}/\text{Sb}^{3+}$ combination.

Each Ga/Sb tetranuclear heterometallic cluster is linked to four adjacent clusters through their four terminal sulfurs, resulting in a 2D anionic network of $[\text{Ga}_2\text{Sb}_2\text{S}_7]^{2-}$ along the *ab* plane (Figure 1b). The 2D network of **1** features a grid layer with eight-membered rings composed of four GaS_4 tetrahedra and four SbS_3 trigonal pyramids. The adjacent layers are stacked in an AAA sequence along the *c* axis. The interlayer distance is estimated to be 9.46 Å. The lone-pair electrons of the Sb^{III} atoms are oriented toward the interlayer spaces. $[\text{Ni}(\text{en})_3]^{2+}$ complexes as template molecules and charge-balancing agents are located at the interlayer spaces and form extensive $\text{N-H}\cdots\text{S}$ hydrogen bonds with the S atoms of the anionic layer. The $\text{N-H}\cdots\text{S}$ hydrogen-bond distances and angles fall in the range of 3.272(6)–3.740(7) Å and 126.5–154.1°, respectively. Hence, the interconnection of the inorganic anionic layers with the template cations via hydrogen bonds results in a 3D network (Figure 2).

When dimethylammonium in situ synthesized by DMF was used as the template, **2** was isolated. The structure of **2** consists of a $[\text{Ga}_2\text{Sb}_2\text{S}_7]^{2-}$ layer similar to those in **1**. The coordination geometries around the Ga and Sb ions are similar to that in **1** (Figure S2 in the Supporting Information). The template cation ($[(\text{Me})_2\text{NH}_2]^+$) is also involved in hydrogen bonding (Figure S3 and Table S4 in the Supporting

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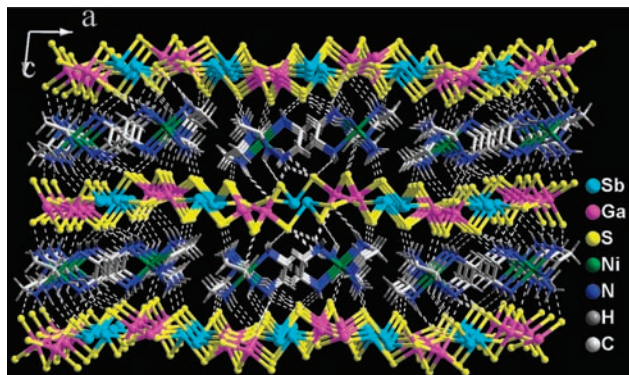


Figure 2. Packing of layers in **1** in a perspective view along the *b* axis. Dotted lines show the extensive N–H⋯S hydrogen bonds in the structure.

Information). However, the interlayer distance of ~ 7.78 Å in **2** is significantly smaller than that of **1**.

The thermal stabilities of **1** and **2** were examined by thermogravimetric analysis (TGA) in a N_2 atmosphere from 30 to 500 °C. TGA curves for **1** and **2** are shown in Figures S7 and S8 in the Supporting Information. **1** is stable up to 240 °C. Then the TGA curve of **1** displays one main step of weight loss from 240 to 500 °C, which corresponds to the loss of organic amine molecules. The observed weight loss of 22.7% is close to the theoretical value of 21.3%. From 30 to 500 °C, **2** lost a total weight of 17.5% (theoretical value of 17.7%), which can be attributed to the removal of two dimethylamine molecules and one H_2S molecule per formula.

The optical diffuse-reflectance spectra of **1** and **2** measured at room temperature are plotted in Figure 3. The optical absorption edges of **1** and **2** are found to be 1.97 and 2.05 eV, respectively, which lie in the energy range suitable for visible-light photocatalytic applications.^{1d} Compared with the bulk Ga_2S_3 (3.3 eV),¹² there is a noticeable red shift of the absorption edges, whereas those of other organically templated gallium sulfides exhibit a blue shift.¹³ There is a blue shift of their absorption edges in contrast with the bulk Sb_2S_3 (1.6 eV).¹⁴ It is seemingly dictated by a hybrid of the GaS_4

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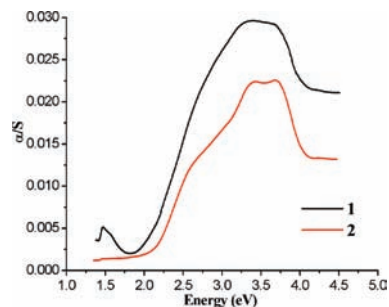


Figure 3. Solid-state optical absorption spectra of **1** and **2**.

and SbS_3 components. This indicates that the current compounds are good examples of the composition, structure, and property correlation. In addition, the peak at 1.47 eV in the diffuse-reflectance spectrum of **1** presumably arises from a d–d electronic transition of Ni^{2+} ion in octahedral coordination.

In conclusion, we have presented that two gallium antimony sulfides have been solvothermally synthesized and structurally, thermally, and optically characterized. It is interesting to combine GaS_4 tetrahedra and SbS_3 asymmetric coordination geometries in a single-crystal structure to form a novel heterometallic cluster of $\{Ga_2Sb_2S_9\}$, which endues a new SBU of chalcogenides. This suggests that many new gallium antimony sulfides with structural diversity and interesting optical and electronic properties can be developed by using the synthetic strategy applied here.

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Supporting Information Available: Crystallographic data in CIF format and tables of bond lengths and angles, IR, TGA, and powder X-ray diffraction patterns. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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