

Quaternary Tin(IV) Antimony(III) Sulfide Decorated with Lanthanum(III) Ethylenediamine Complexes: $[\text{La}(\text{en})_4\text{SbSnS}_5]_2 \cdot 0.5\text{H}_2\text{O}$

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A quaternary tin(IV) antimony(III) sulfide decorated by lanthanum(III) ethylenediamine complexes, namely, $[\text{La}(\text{en})_4\text{SbSnS}_5]_2 \cdot 0.5\text{H}_2\text{O}$ (1; en = ethylenediamine), has been solvothermally synthesized and structurally, thermally, and optically characterized. Its structure features an isolated hexanuclear molecule of $[\text{La}(\text{en})_4\text{SbSnS}_5]_2$. The intermolecule hydrogen-bond interactions result in a three-dimensional supramolecular network, which remains intact upon dehydration.

Multinary metal chalcogenides constructed by the combination of main-group (or transition-metal) ions and rare-earth metal ions are of interest in solid-state chemistry because of their fascinating architectures and promising physical properties.^{1–3} The majority of them involve pure inorganic ternary or quaternary compounds such as $\text{Eu}_5\text{Sn}_3\text{S}_{12}$,⁴ $\text{K}_2\text{La}_2\text{Sb}_2\text{S}_9$,⁵ and $\text{EuCu}_2\text{SnS}_4$.² On the other hand, a variety of chalcogenide-based organic–inorganic hybrid compounds with the incorporation of organic species such as organic amines have attracted increasing attention because they may engender new useful properties. In such hybrid compounds, the organic species may play two different roles in terms of the interactions between organic and inorganic components. One is to enter the structures through either ionic bonding or relatively weak hydrogen-bonding

and van der Waals interactions.⁶ The other is to form organic–inorganic covalent architectures via covalent interactions, which can change or modify the physical properties such as optical absorption edges.⁷ To date, many main-group/transition-mixed-metal chalcogenides with covalently bonded organic amines have been reported.^{8,9} In the case of rare-earth-based hybrid mixed-metal chalcogenides, some examples containing rare-earth metal amine complexes as templates interacting with chalcogenide frameworks by hydrogen-bonding have been reported,^{10–12} whereas only several hybrid compounds with organic amines covalently bonded to the chalcogenide moieties have been isolated, which include $[\text{Sm}(\text{en})_3(\text{H}_2\text{O})(\mu\text{-Sb}^{\text{V}}\text{S}_4)]_\infty$ ¹⁰ and $[\text{Ln}(\text{en})_3(\text{H}_2\text{O})_x(\mu_{3-x}\text{-Sb}^{\text{V}}\text{S}_4)]_\infty$ (Ln = La, $x = 0$; Ln = Nd, $x = 1$).¹³ However, they are only limited to the ternary metal chalcogenide systems of $\text{L–Ln–Sb}^{\text{V}}$ (or Sn, Ga)–S (L = organic amines). The synthesis of rare-earth-based multinary chalcogenides modified with organic components remains a big challenge because the complexes formed by rare-earth metal ions with sulfur, selenium, and tellurium are generally comparatively unstable with respect to heat, water, oxygen, and light sensitivity.¹⁴

One of our recent research interests is focused on the development of novel organic–inorganic hybrid heterometallic

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chalcogenides by integrating asymmetric coordination polyhedra of Sb^{III} with other metal polyhedra such as main-group metal tetrahedra or rare-earth metal polyhedra in the presence of various organic amines or $[\text{M}(\text{amine})_m]^{n+}$ (M = transition or rare-earth metal) complexes. Such an approach would lead to the formation of various heterometallic secondary building units (SBUs), further generating novel chalcogenides,^{15,16} because the asymmetric coordination geometry adopted by Sb^{III} with stereochemically active lone-pair electrons can induce noncentrosymmetric structures, which might engender interesting physical properties such as second harmonic generation.¹⁷ Here we present a novel quaternary tin(IV) antimony(III) sulfide decorated by lanthanum(III) ethylenediamine complexes, namely, $[\text{La}(\text{en})_4\text{SbSnS}_5]_2 \cdot 0.5\text{H}_2\text{O}$ (**1**).

1 was prepared from a mixture of Sb, Sn, S, and La (CH_3COO)₃ · 5H₂O in ethylenediamine, which was sealed in a stainless steel reactor with a 20 mL Teflon liner and heated at 160 °C for 7 days. The product consisted of orange crystals of **1** and a small amount of indefinite light-yellow powders. Single-crystal X-ray crystallography¹⁸ reveals that the structure of **1** features an isolated hexanuclear molecule of $[\text{La}(\text{en})_4\text{SbSnS}_5]_2$ constructed by two asymmetric units related via an inversion center located at the center of the $\text{Sb}_2\text{Sn}_2\text{S}_4$ ring. The asymmetric unit of **1** contains one crystallographically independent La^{3+} ion, one Sb^{3+} ion, one Sn^{4+} ion, five S^{2-} ions, four ethylenediamine molecules as ligands, and a quarter of a lattice water molecule (Figure S1 in the Supporting Information). The Sn^{4+} ion is surrounded by four S^{2-} ions to form a $\{\text{SnS}_4\}$ tetrahedron, and the $\text{Sn}-\text{S}$ bond lengths fall in the range of 2.3224(17)–2.4447(16) Å. The Sb^{3+} ion adopts a $\{\text{SbS}_3\}$ trigonal-pyramidal asymmetric coordination geometry with $\text{Sb}-\text{S}$ bond lengths of 2.3396(17), 2.4793(17), and 2.5178(15) Å. The La^{3+} ion is nine-coordinated with one sulfur anion and eight amino nitrogen donors of four bidentate ethylenediamine ligands and conforms most closely to a distorted tricapped trigonal prism of $\{\text{LaSN}_8\}$ (Figure 1a). The $\text{La}-\text{S}$ bond distance is 3.0424(16) Å, and the $\text{La}-\text{N}$ bond distances vary from 2.683(5) to 2.797(5) Å, which are comparable to those in $[\text{La}(\text{en})_3(\mu_3-\text{Sb}^{\text{V}}\text{S}_4)]_\infty$.¹³ Both S1 and S5 are unidentate terminal ligands, while S2, S3, and S4 all act as bidentate metal linkers. S2 and S4 bridge to one Sb^{3+} ion and one Sn^{4+} ion, respectively, whereas S3 links one La^{3+} ion and one Sn^{4+} ion. Two $\{\text{SbS}_3\}$ trigonal pyramids and two $\{\text{SnS}_4\}$ tetrahedra share four corners (two S2 and two S4) to form a SBU with stoichiometry of $\{\text{Sn}_2\text{Sb}_2\text{S}_{10}\}$, in which there exists an eight-membered ring of $\text{Sb}_2\text{Sn}_2\text{S}_4$. Similar structural units were observed in some mixed-metal chalcogenides, such as $[\text{Mn}(\text{C}_6\text{H}_{18}\text{N}_4)]_4\text{Mn}_2\text{Sb}_4\text{S}_{12}$ and $[\text{Fe}(\text{C}_6\text{H}_{18}\text{N}_4)]\text{FeSbS}_4$.⁹ It is noteworthy that such a SBU is similar to the newly reported

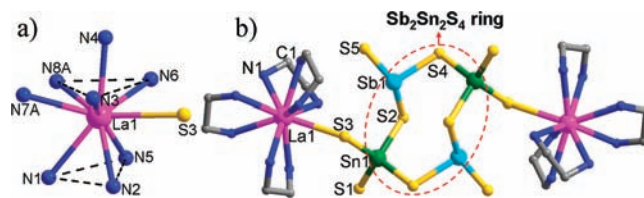


Figure 1. (a) Coordination environment of the La^{3+} ion. (b) Hexanuclear molecule of $[\text{La}(\text{en})_4\text{SbSnS}_5]_2$ constructed by two asymmetric units related via an inversion center located at the center of the $\text{Sb}_2\text{Sn}_2\text{S}_4$ ring. Hydrogen atoms are omitted for clarity.

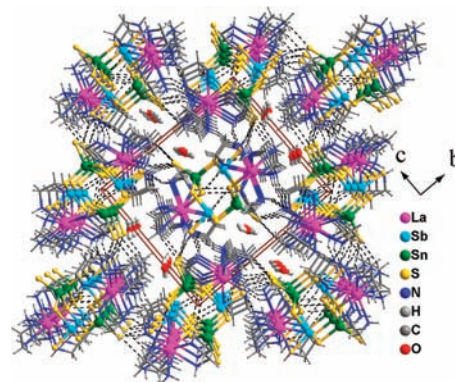


Figure 2. Perspective view of a 3D network formed by the hydrogen-bonding interactions among the hexanuclear molecules along the a axis.

tetranuclear heterometallic cluster $\{\text{Ga}_2\text{Sb}_2\text{S}_9\}$,¹⁶ which is also composed of two metal tetrahedra and two $\{\text{SbS}_3\}$ trigonal pyramids. However, it is different in that the two $\{\text{GaS}_4\}$ tetrahedra share a $\mu_2-\text{S}$ atom in $\{\text{Ga}_2\text{Sb}_2\text{S}_9\}$, whereas there is no bridging sulfur atom between the two $\{\text{SnS}_4\}$ tetrahedra in $\{\text{Sn}_2\text{Sb}_2\text{S}_{10}\}$ (Figure S2 in the Supporting Information). As a result, the $\{\text{Ga}_2\text{Sb}_2\text{S}_9\}$ cluster is asymmetric, while the $\{\text{Sn}_2\text{Sb}_2\text{S}_{10}\}$ cluster is centrosymmetric.

Then the $\{\text{Sn}_2\text{Sb}_2\text{S}_{10}\}$ unit is further decorated with two lanthanum(III) ethylenediamine complexes via two S3 bridging atoms. Thus, an isolated hexanuclear molecule of $[\text{La}(\text{en})_4\text{SbSnS}_5]_2$ is generated (Figure 1b), which obviously differs from the reported ternary hybrids of $[\text{Sm}(\text{en})_3(\text{H}_2\text{O})-(\mu-\text{Sb}^{\text{V}}\text{S}_4)]_\infty$ ¹⁰ and $[\text{Ln}(\text{en})_3(\text{H}_2\text{O})_x(\mu_{3-x}-\text{Sb}^{\text{V}}\text{S}_4)]_\infty$ ($\text{Ln} = \text{La}$, $x = 0$; $\text{Ln} = \text{Nd}$, $x = 1$).¹³ Their structures all feature neutral one-dimensional chains constructed by rare-earth ethylenediamine complexes and multidentate $\{\text{Sb}^{\text{V}}\text{S}_4\}$ tetrahedra. To the best of our knowledge, the title compound is the first quaternary main-group mixed-metal sulfide decorated by rare-earth organic amine complexes. Each neutral isolated hexanuclear molecule interacts with neighboring molecules via intermolecular $\text{N}-\text{H} \cdots \text{S}$ hydrogen bonds, resulting in a three-dimensional (3D) supramolecular network (Figure 2). The lattice water molecules are located at the channels along the a axis. The $\text{N} \cdots \text{S}$ distances are in the range of 3.375(6)–3.708(6) Å, and the $\text{N}-\text{H} \cdots \text{S}$ angles vary from 146.9 to 173.2° (Table S2 in the Supporting Information).

The thermal property of **1** was studied by thermogravimetric analysis–differential scanning calorimetry (TGA–DSC) in a N_2 atmosphere from 30 to 500 °C. TGA and DSC curves for **1** are shown in Figure 3a. The TGA curve revealed that **1** lost the lattice water molecules below 200 °C with a mass loss of 0.56%, which was close to the theoretical value of 0.57%. In the range of 200–400 °C, the ethylenediamine ligands were removed in two steps with a total

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(18) Crystal data for **1**: $\text{C}_{16}\text{H}_{65}\text{La}_2\text{N}_{16}\text{O}_{50}\text{S}_{10}\text{Sb}_2\text{Sn}_2$, $M = 1569.14$, monoclinic, $P2_1/n$, $a = 10.801(4)$ Å, $b = 16.336(5)$ Å, $c = 14.311(5)$ Å, $\beta = 99.107(7)^\circ$, $V = 2493.3(14)$ Å³, $Z = 2$, $D_{\text{calc}} = 2.090$ g cm⁻³, $F(000) = 1506$, $\mu = 4.182$ mm⁻¹, $T = 293(2)$ K, 18 847 reflections measured, 5698 unique reflections ($R_{\text{int}} = 0.0573$), 5002 observed reflections [$I > 2\sigma(I)$] with $R1$ ($wR2$) = 0.0440 (0.0968), $R1$ ($wR2$) = 0.0518 (0.1027) (all data), $\text{GOF} = 1.127$. CCDC 730339.

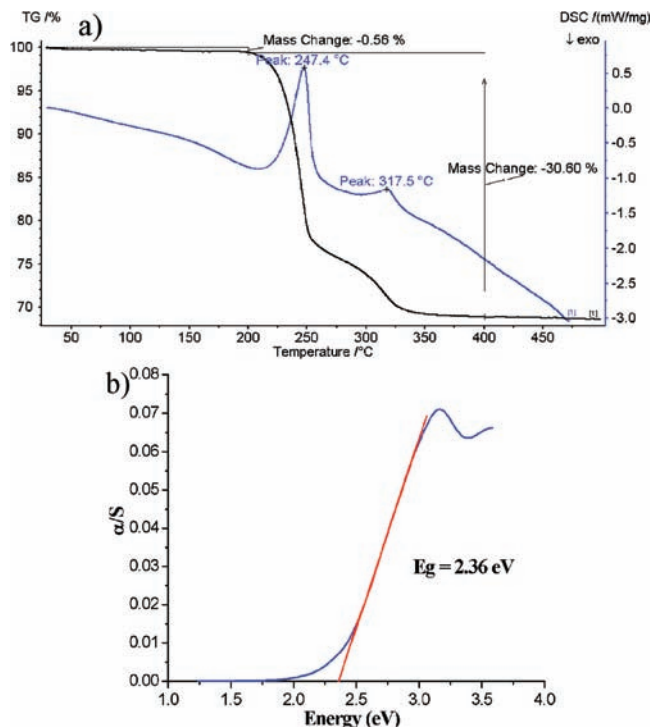


Figure 3. (a) TGA (black) and DSC (blue) curves for **1**. (b) Solid-state optical absorption spectrum of **1**.

observed weight loss of 30.6% in accordance with the theoretical value of 30.6%. There were two accompanying endothermic signals at 247.4 and 317.5 °C on the DSC curve, respectively.

To further explore whether the host 3D supramolecular framework would break down upon removal of the lattice water molecules, the crystalline sample of **1** was heated at 170 °C for 15 min in the TGA system. Single-crystal X-ray crystallography¹⁹ of the residue crystal (**1'**) confirms that the 3D supramolecular framework does not change or collapse after removal of the lattice water molecules. Moreover, the shape and color of the dehydrated crystals almost retain the pristine ones. Single-crystal X-ray crystallography of **1'**

(19) Crystal data for **1'**: C₁₆H₆₄La₂N₁₆S₁₀Sb₂Sn₂, *M* = 1560.13, monoclinic, *P*2₁/*n*, *a* = 10.7818(9) Å, *b* = 16.3090(17) Å, *c* = 14.2616(13) Å, β = 98.996(4)°, *V* = 2476.9(4) Å³, *Z* = 2, *D*_{calc} = 2.092 g cm⁻³; *F*(000) = 1496, μ = 4.208 mm⁻¹, *T* = 293(2) K, 18 897 reflections measured, 5662 unique reflections (*R*_{int} = 0.0518), 4912 observed reflections [*I* > 2σ(*I*)] with *R*1 (*wR*2) = 0.0427 (0.0813), *R*1 (*wR*2) = 0.0524 (0.0859) (all data), *GOF* = 1.104, CCDC 734066.

reveals that its cell parameters are slightly smaller than those of the pristine **1**. It is worth noting that this is the first example of the host framework remaining intact after dehydration in the metal chalcogenide system, although some compounds with similar phenomena have been reported in other materials.²⁰

The optical diffuse-reflectance spectrum of **1** measured at room temperature is plotted in Figure 3b. The obtained absorption versus energy spectrum shows the optical band gap at 2.36 eV for **1**, which suggests that the title compound is a semiconductor. Its band gap falls in between those of [La(en)₃(μ₃-SbS₄)]_∞ (2.29 eV)¹³ and [Sm(en)₃(H₂O)(μ-SbS₄)]_∞ (2.75 eV),¹⁰ [Nd(en)₃(H₂O)(μ₂-SbS₄)]_∞ (3.68 eV).¹³

In conclusion, although some ternary L–Ln–Sb (or Sn, Ga)–S systems have been reported, hitherto no quaternary metal chalcogenide incorporating covalently bonded rare-earth metal amine complexes has been isolated. Here a quaternary tin(IV) antimony(III) sulfide decorated by lanthanum(III) ethylenediamine complexes has been solvothermally synthesized and structurally, thermally, and optically characterized. It is interesting to first combine the {LaSN₈} polyhedra, {SnS₄} tetrahedra, and {SbS₃} trigonal pyramids into a neutral hexanuclear molecule of [La(en)₄-SbSnS₅]₂, which endues a new SBU of multinary chalcogenides. Moreover, the host 3D supramolecular framework of **1** remains intact upon dehydration. The current compound provides a synthetic route for the quaternary L–Ln–Sn–Sb–S system as a new member of the metal chalcogenide family.

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Supporting Information Available: Crystallographic data in CIF format, tables of bond lengths and angles and hydrogen bonds, additional structural figures, additional synthetic details, an IR spectrum, 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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