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$[Ni(dien)_2]_3[Ge_3Sb_8S_{21}]\cdot 0.5H_2O$: A new 2-D layered thiogermanate–thioantimonate with metal complexes as template ions

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ABSTRACT

A new 2-D layered thiogermanate–thioantimonate $[Ni(dien)_2]_3[Ge_3Sb_8S_{21}]\cdot 0.5H_2O$ (**1**, dien = diethylenetriamine) was synthesized under solvothermal conditions and structurally characterized. The polymeric $[Ge_3Sb_8S_{21}]^{6n-}{}_n$ anion in **1** is composed of heterometallic semicube $[GeSb_2S_7]$ clusters and trigonal-pyramidal $[SbS_3]$ units, which are interconnected to build a 2-D layer with the large $Sb_{18}S_{18}$ heterorings. The apertures of the $Sb_{18}S_{18}$ heterorings are filled by three $[Ni(dien)_2]^{2+}$ complex cations as template ions. The absorption band edge of **1** is 2.29 eV, exhibiting properties of the semiconductor.

Chalcogenidogermanates are of interest in solid-state chemistry because of their fascinating architectures and potential applications in thermoelectricity, ionic conductivity, gas separation, phase-change memory, optical property and photocatalysis [1]. In the chalcogenidogermanate family, significant progress has already been made in the synthesis of open framework thiogermanates by mild solvothermal methods in the presence of tetraalkylammonium hydroxides or nonchelating amines. Various open frameworks are usually built up from the $[M_yGe_{4-y}S_{10}]^{4-}$ ($y = 0$–3) adamantane-like units as secondary building units, which are mostly constructed by the $[GeS_4]$ tetrahedral units or the combination of $[GeS_4]$ and other $[MS_4]$ ($M = $ Ga, In) tetrahedral units [1d,2]. However, relatively few thiogermanates containing non-tetrahedral atoms have been reported [3]. The antimony is of specific interest and tends to adopt the non-tetrahedral coordination geometries of $[SbQ_x]$ ($Q = $ S, Se, Te; $x = 3$–5) [4], which can induce noncentrosymmetric structures with interesting physical properties, such as second-harmonic generation [5]. The integration of non-tetrahedral $[SbS_x]$ into thiogermanate frameworks would likely result in a new class of materials with useful properties. But the thiogermanates containing non-tetrahedra of Sb^{3+} under mild solvo-(hydro) thermal conditions are less explored [3b–e]. The combination of Ge and Sb in thiometalates is difficult to achieve, which is more likely that suitable dissolved Ge/Sb species are present in different concentrations and a differing tendency of the species to condensate.

Metal complexes (MCs) instead of organic amines or tetraalkylammonium ions as structure-directing agents or templates have been proved to be very effective in the syntheses of metal chalcogenides, because some of them are chiral complexes, which can imprint their chiral characters into the inorganic host *via* the H-bonding interactions [6]. In employing MCs as the structure-directing agents or templates, a number of thioantimonates {such as $[Co(en)_3][CoSb_4S_8]$ [7], $[Co(en)_3][Sb_{12}S_{19}]$ [8], $[M(en)_3]Sb_2S_4$ ($M = $ Co, Ni) [9], $[M(en)_3]Sb_4S_7$ ($M = $ Fe, Ni) [9], $[Mn(tren)]_2Sb_2S_5$ [10], $[Mn(tren)]_2Mn_2Sb_4S_{10}$ [10], and $[Ni(phen)_3]_2Sb_{18}S_{29}$ [11]} and thiogermanates {such as $[Ge_3S_9Zn_2(H_2O)_2][Zn(tren)(H_2O)]$ [12], $[M(en)_3]_2Ge_2S_6$ ($M = $ Mn, Ni) [13], $[Ni(dien)_2]_2(Ge_2S_6)$ [14], $[Ni(dien)_2](H_2pipe)(Ge_2S_6)$ [14], $\{[Mn(tren)]_2(Ge_2S_6)\}$ [14], $\{[M(tepa)]_2(Ge_2S_6)\}$ ($M = $ Mn, Ni) [14], and $[M(dap)_3]_4Ge_4S_{10}Cl_4$ ($M = $ Co, Ni) [15]} have been made. However, little attention has been paid to the possibility of using MCs as the structure-directing agents or templates in making thiogermanate–thioantimonates; the limited examples include $[M(en)_3][GeSb_2S_6]$ ($M = $ Ni, Co, Ge) [3d–e]. More recently, we have attempted the preparation of thiogermanate–thioantimonates by using MCs as the structure-directing agents or templates, which have successfully made two thiogermanate–thioantimonates $[Mn(en)_3]GeSb_2S_6$ and $[Co(dien)_2]_2GeSb_4S_{10}$ [3c]. As part of the continuing work in this system, herein we reported the solvothermal syntheses, structure, and characterization of one new thiogermanate–thioantimonate $[Ni(dien)_2]_3[Ge_3Sb_8S_{21}]\cdot 0.5H_2O$ (**1**, dien = diethylenetriamine), where the $[Ni(dien)_2]^{2+}$ cations reside in the cavities of the 2-D $[Ge_3Sb_8S_{21}]^{6n-}{}_n$ layer. Although some layered thioantimonates with MCs have been reported [7,16], MCs are

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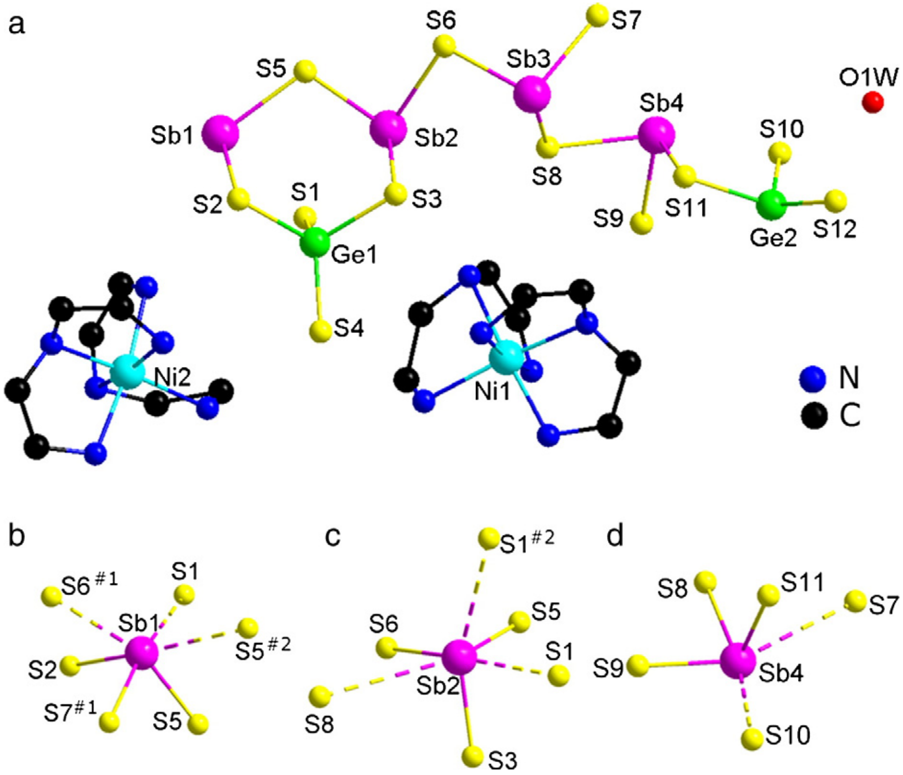

Fig. 1. a) An asymmetric unit of **1**. All H atoms have been omitted for clarity. b–d) The coordination environment of Sb1, Sb2 and Sb4 atoms [symmetry operation: (#1) 0.5 + x, 0.5 + y, z; (#2) 1 − x, y, 1 − z].

usually sandwiched between the anionic layers, fulfilling the charge-balancing role.

Yellow block crystals of **1** were obtained by solvothermal reaction of GeO_2, Sb, S, Co and dien (2.0 mL) at 170 °C for 10 days [17]. The amount of Sb in **1** is much more than those of other solid reactants [3b–e], resulting in the formation and crystal growth of a new thiogermanate–thioantimonate phase. **1** crystallizes in the monoclinic space group $C2/m$ with four formula units in the unit cell [18] and consists of porous 2-D $[Ge_3Sb_8S_{21}]^{6n-}{}_n$ anionic layers, $[Ni(dien)_2]^{2+}$ complex cations and free water molecules (Fig. 1). The Sb atom

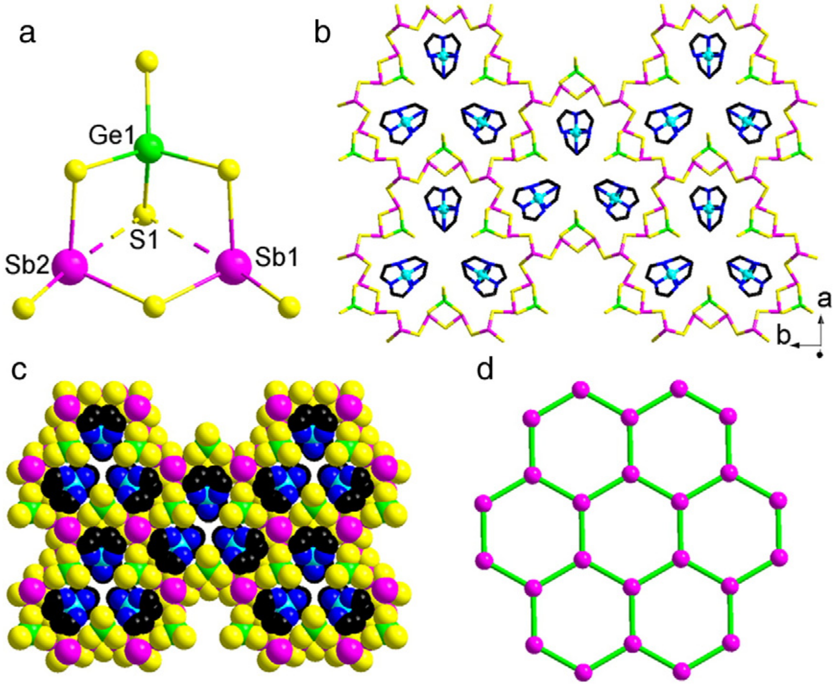

Fig. 2. a) Heterometallic semicube $[GeSb_2S_7]$ cluster; b) view of 2-D anionic $[Ge_3Sb_8S_{21}^{16-}]_n$ layer, showing that cations are located in the apertures of the $Sb_{18}S_{18}$ hetero-rings; c) Space-filling representation of 2-D anionic $[Ge_3Sb_8S_{21}^{16-}]_n$ layer and $[Ni(dien)_2]^{2+}$ cations; d) topology of the layer [pink: trigonal-pyramidal $[SbS_3]$ nodes].