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$[M(dap)_3]InSb_3S_7$ (M = Co, Ni): Two Novel Open-Framework Thioindate−Thioantimonates with 8-, 12-, and 16-Ring Intersecting Channels

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Two novel open-framework thioindate−thioantimonates $[M(dap)_3]InSb_3S_7$ [M = Co(**1**), Ni (**2**); dap = 1,2-diaminopropane] have been solvothermally synthesized and structurally characterized. **1** and **2** consist of InS_4 tetrahedra and SbS_3^{3-} trigonal pyramids, which are interconnected to form the first examples of three-dimensional In−Sb−S open frameworks with 8-, 12-, and 16-ring intersecting channels.

Since their discovery by Bedard and co-workers in 1989,[1] open-framework chalcogenides have raised increasing interest because of their potential as next-generation zeolites, capable of integrating conventional zeolite functionality with optical, electronic, and electrooptic properties of metal chalcogenides.[2] Nowadays, great progress has been made in the synthesis of open-framework thioindates.[3] Most of these open frameworks are constructed by building units involving only both InS_4 and other MS_4 tetrahedra [M = group 13 (Ga),[3j] group 14 (Ge, Sn),[3b,p] and some transition-metal elements[3d−k]]. In contrast, relatively few thioindates containing other polyhedral atoms have been reported.[4] The Sb element is a promising candidate for other polyhedral atoms because it tends to adopt the asymmetric coordination geometries of SbQ_x (Q = S, Se, Te; $x = 3-5$) units, which can induce noncentrosymmetric structures with interesting physical properties, such as second-harmonic generation.[5] As expected, the incorporation of a Sb atom into a pure thioindate framework would likely result in a new class of materials with novel topologies and useful properties. However, there is little research carried out on the In−S−Sb system under mild solvo(hydro)thermal conditions; the limited examples include one-dimensional (1D) chain $[Ni(dien)_2]_2In_2Sb_4S_{11}$,[6] two-dimensional (2D) layer $[(CH_3CH_2CH_2)_2NH_2]_5In_5Sb_6S_{19}\cdot 1.45H_2O$,[4b] and 2D layer $[Ni(dien)_2]_3(In_3Sb_2S_9)_2\cdot 2H_2O$,[6] in which organic amines or complex cations play an important structure-directing role in the formation of thioindate−thioantimonates. Unexpectedly, however, no three-dimensional (3D) thioindate−thioantimonates with open frameworks have been reported to date. In this work, we present the synthesis and characterization of the first truly 3D thioindate−thioantimonates $[M(dap)_3]InSb_3S_7$ [M = Co (**1**), Ni (**2**); dap = 1,2-diaminopropane], where InS_4 tetrahedra and acentric SbS_3^{3-} units are interconnected to form a 3D In−Sb−S open framework with 8-, 12-, and 16-ring intersecting channels.

The light-yellow block crystals of **1** and **2** were obtained by the solvothermal reaction of In, Sb, Co (or Ni), and S in a mixed solvent of dap and H_2O at 170 °C.[7] The compounds are stable under ambient conditions and are insoluble in any solvents. **1** and **2** are isostructural, and only **1** is discussed here in detail. The structure of **1** consists of a 3D polymeric

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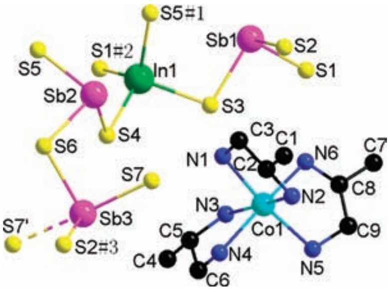

Figure 1. Crystal structure of **1**, with the S7 atom being disordered. [Symmetry operation: #1, 2 − *x*, −*y*, −*z*; #2, 1 − *x*, −*y*, −*z*; #3, 1 + *x*, −0.5 − *y*, 0.5 + *z*]. All H atoms are omitted for clarity.

$[InSb_3S_7^{2-}]_n$ anion and charge-compensating $[Co(dap)_3]^{2+}$ cations (Figures 1 and S1 in the Supporting Information, SI). The In atom is coordinated with four S atoms to form a slightly distorted tetrahedral InS_4. The In−S bond lengths vary from 2.440(6) to 2.457(5) Å, comparable with those reported for other thioindates.[3] Both Sb1 and Sb2 atoms are coordinated with three S atoms to give a pyramidal SbS_3. The interatomic distances and angles are in the typical range of those for the well-known SbS_3 trigonal pyramid reported in the literature.[8] The S7 atom is disordered, with the occupancy of the disordered S7/S7′ atom assigned as 0.51/0.49, resulting in the Sb3 atom adopting a *psi*-SbS_4 pseudotrigonal bipyramid. Two InS_4 tetrahedra and two SbS_3 trigonal pyramids are interconnected to yield an eight-membered $In_2Sb_2S_4$ ring in a chairlike conformation, which is further joined at the In atom to generate the infinite anionic $[In_2Sb_2S_8^{4-}]_n$ chain along [100] (Figure S2a in the SI). There are two kinds of In···In distances (5.84 and 5.52 Å) in $In_2Sb_2S_4$ rings. The repeating unit containing two $In_2Sb_2S_4$ rings with a period of 10.72 Å is equal to the unit cell *a* axis and is less than the sum of the two In···In distances (11.36 Å). This chain is markedly different from other thioarsenate−antimonate chains with a chairlike $M_2M'_2S_4$ cluster (Figure S2b in the SI), as exemplified by $[Sb_2S_4^{2-}]_n$,[9] $[InAsS_4^{2-}]_n$,[4c] and $[FeSbS_4^{2-}]_n$,[10] which can be viewed as a string of fused eight-membered $M_2M'_2S_4$ rings and four-membered M_2S_2 rings in an alternating fashion. On the basis of valence sum calculations,[11] the oxidation state of the one In atom is 3+, and those of all of the Sb atoms are 3+.

The adjacent $[In_2Sb_2S_8^{4-}]_n$ chains are aligned in an antiparallel fashion, which is linked by *psi*-SbS_4 units to give a 2D layer in the (010) plane (Figure S3 in the SI). These layers are stacked along the *c* axis in an −ABA− sequence and are further bridged by *psi*-SbS_4 units to lead to the formation of the final 3D $[InSb_3S_7^{2-}]_n$ framework with 3D intersecting channels (Figure 2a). Along the [100] direction, the openings of the 16-ring channels are elliptical in shape and delimited by 12 SbS_3 trigonal pyramids and 4 InS_4 tetrahedra with an approximate free-pore diameter of 7.90 × 16.45 Å^2 (Figure S4a,b in the SI). The terminal S atom of the SbS_3 trigonal pyramid protrudes into the 16-ring channel. Each 16-ring channel is surrounded by eight neighboring 16-ring channels. Each pore wall of the 16-ring channels is built from two 12-ring windows with the $InS_4-(SbS_3)_3-InS_4-SbS_3-InS_4-(SbS_3)_3-InS_4-SbS_3$ sequence along the [011] and [0−11] directions, respectively (Figure S4c,d in the SI). $[Co(dap)_3]^{2+}$ cations reside in the 16-ring channels, and the CH_3- groups of some of the dap ligands protrude through the 12-ring channels, which compensate for the negative charge of the 3D $[InSb_3S_7^{2-}]_n$ anion. $[Co(dap)_3]^{2+}$ cations with both $\Delta(\delta\delta\lambda)$ and $\Lambda(\lambda\lambda\delta)$ conformations are present as a result of the centrosymmetric nature of the structure. Distances between the N atoms in $[Co(dap)_3]^{2+}$ and the S atoms in the 3D $[InSb_3S_7^{2-}]_n$ framework lie in the range 3.11(3)−3.64(2) Å (Table S3 in the SI), suggesting a hydrogen-bonding interaction between the cations and the anionic framework.[12] A *PLATON* analysis,[13] performed only on the framework structure, suggested a solvent-accessible volume of approximately 45.1%. The network topology of the 3D framework can be simplified by considering the InS_4 tetrahedra as 4-connected nodes, the SbS_3 trigonal pyramids as 3-connected nodes, and the *psi*-SbS_4 units as linkers. As a result, a previously unknown framework topology with the total Schläfli symbol of $(4 \times 10^2)(4^2 \cdot 10^4)$ and the long vertex symbol of $(4 \cdot 10_4 \cdot 10_4)(4 \cdot 4 \cdot 10_4 \cdot 10_4 \cdot 10_4 \cdot 10_4)$ is formed (Figure 2b).

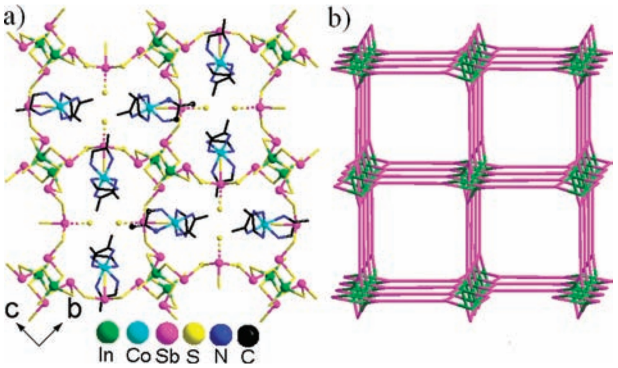

Figure 2. (a) 3D network built by 2D layers and SbS_3 trigonal pyramids, showing the location of complex $[Co(dap)_3]^{2+}$ cations. All H atoms are omitted for clarity. (b) Framework topology of **1** (green/magenta: InS_4 tetrahedral/SbS_3 trigonal pyramid nodes).

Another unique structural feature of **1** is that it contains two types of helical 8-ring channels along the [001] direction (Figure S5a in the SI). The 8-ring helical channels with opposite chirality are triangular in shape (Figure S5b−e in the SI). The period of the helix is 16.4 Å by the centroid of In atoms. Furthermore, two other types of helical 8-ring channels can also be observed in the [010] direction (Figure S5f in

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(7) Synthesis of **1**: The reagents of In (0.013 g), S (0.096 g), Sb (0.121 g), Co (0.058 g), dap (2 mL), and H_2O (0.2 mL) were placed in a thick Pyrex tube (ca. 20 cm long). The sealed tube was heated at 170 °C for 15 days to yield light-yellow block-shaped crystals. The crystals were washed with ethanol, dried, and stored under vacuum (27% yield based on In). Elem anal. Calcd: C, 10.97; H, 3.07; N, 8.53. Found: C, 10.91; H, 3.13; N, 8.56. Synthesis of **2**: The light-yellow crystals of **2** were prepared by a method similar to that used in the synthesis of the crystals of **1** except that Co powder was replaced by Ni powder (yield 42%, based on In). Elem anal. Calcd: C, 10.97; H, 3.07; N, 8.53. Found: C, 10.93; H, 3.12; N, 8.55. IR data of **1** and **2** are given in the Supporting Information. The CCDC reference numbers for **1** and **2** are 800560 and 800561, respectively.

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the SI), which are similar to those in the [001] direction, only differing in their shape and size (Figure S5g−h in the SI). Among the 3D thioantimonates, the helical 8-ring channels are very rare and are only observed in the 3D $[(Me)_2NH_2]_2[GeSb_2S_6]$.[14]

The use of transition-metal complexes (TMCs) as template agents has several distinct features. Among them, the most important one is integration of the electronic, optical, and magnetic properties of TMCs with the host inorganic framework. However, the template effect of TMCs has to be proven, which indeed is not easy mainly because chalcogenidometalates prepared by solvothermal methods commonly exhibit low-dimensional structures with an increase in the size of the TMCs, which might be apt to break off some linkages and create larger spaces for themselves, such as the space between molecules, chains, or layers.[15] In the presence of larger TMCs such as counterions, the thioindate anions generally adopt a 1D $[InS_2]_n$ structure,[16,17] while the thioantimonate anions usually display oligomeric (such as $[Sb_2S_5]^{4-}$,[18] $[Sb_3S_6]^{3-}$,[19] and $[Sb_4S_8]^{4-}$[20]), 1D chain (such as $[Sb_4S_8{}^{4-}]_n$,[21] $[Sb_4S_7{}^{2-}]_n$,[15,22] and $[Sb_4S_9{}^{4-}]_n$[23]), and 2D layer (such as $[Sb_4S_7{}^{2-}]_n$[24,25] and $[Sb_{22}S_{42}{}^{18-}]_n$[26]) structures. However, the 3D thioindate−thioantimonate anions with larger TMCs are very scarce; the limited examples include $[Sb_{12}S_{19}{}^{2-}]_n$,[12] $[Sb_4S_7{}^{2-}]_n$,[27] and $[Sb_{12}S_{21}{}^{6-}]_n$,[24a] where $[SbS_3]^{3-}$ and Ψ-$\{SbS_4\}$ trigonal bipyramids are interconnected to form different 3D thioantimonate frameworks with common 1D closed channels. However, the 3D In−Sb−S frameworks of **1** and **2** possess 1D chirally helical channels with no closed 8-ring, which is distinctly different from the reported 3D thioantimonate framework and represents a new type.

UV−vis absorption spectra of **1** and **2** (Figure S6 in the SI) were calculated from the data of diffuse reflectance using the Kubelka−Munk function.[28] The weak absorptions at 1.82 and 1.86 eV in **1** and **2**, respectively, presumably arise from the d−d electronic transition of previously reported molecular Co^{2+} or Ni^{2+} complexes.[29] The absorption band edges at 3.02 eV for **1** and 2.97 eV for **2** could be attributed to the lowest possible electronic excitation located at the $[InSb_3S_7{}^{2-}]$ anion. This value is very close to those of other indium sulfides, $[Ni(tepa)]_2[In_4S_7(SH)_2]\cdot H_2O$ (3.28 eV)[17] and $[In_8S_{13}(S_3)_{1/2}$-$(SH)][In_4S_6(S_3)_{1/2}(SH)](TMDPH_2)_5$ (3.10 eV),[3n] which exhibit the properties of a wide-band-gap semiconductor. The thermogravimetric (TG) behavior of **1** and **2** was investigated (Figure S7 in the SI). Their TG curves show that similar three-step weight losses (22.14% for **1** and 22.72% for **2**) occur in the range of 240−660 °C, assigned to the removal of the dap ligand (calcd 22.56%). The structures collapsed and converted to an amorphous phase, suggesting that the frameworks of **1** and **2** were not stable to the thermal removal of the dap molecules.

In summary, two novel thioindate−thioantimonates templated by a larger complex cation were synthesized under solvothermal conditions. The previously reported thioindate−thioantimonates with a complex cation[6] were made by a similar method, but they display low-dimensionally different In−Sb−S frameworks, reflecting the structure-directing influence of the different conformations of the $[M(dien)_2]^{2+}$ cations. The formation of 3D extended inorganic structures in **1** and **2** can also be related to the size, shape, and conformation of the $[M(dap)_3]^{2+}$ ions, which are distinctly different from those of the $[M(dien)_2]^{2+}$ ions. Therefore, both **1** and **2** provide the first examples of the linkages of $[InS_4]$ tetrahedra and $[SbS_3]$/[*psi*-SbS_4] units into 3D In−Sb−S open frameworks with large 8-, 12-, and 16-ring intersecting channels. The successful synthesis of **1** and **2** not only enriches the field of metal chalcogenides or thiometalates but also opens the possibility for the solvothermal preparation of other novel open-framework thioindate−thioantimonates with potential catalytic, adsorption, ion-exchange, optical, and electronic properties using different complex cations as templates.

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Supporting Information Available: Crystal data in CIF format, bond lengths and angles, hydrogen bonds, structures, X-ray diffraction data, TG curve, IR data, and energy-dispersive spectrometry and UV−vis spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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