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$[Co(en)_3]CoSb_4S_8$: A Novel Non-Centrosymmetric Lamellar Heterometallic Sulfide with Large-Framework Holes

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Sulfide-based open-framework materials are intriguing compounds. Apart from the fact that they possess a very diverse and therefore interesting structural chemistry, these materials might act as next generation zeolites that combine physical properties typical for semiconductors.[1] The first materials obtained with this in mind, which were based on germanium and tin sulfides, were discovered by Bedard et al. in 1989.[2] Since then, one successful synthetic approach toward this class of compounds has been to generate inorganic frameworks by self-assembly reactions of molecular building blocks (e.g. $[Ge_4S_{10}]^{4-}$ and $[AsS_3]^{3-}$) with metal ions (e.g. Mn^{2+}, Fe^{2+}, Co^{2+}, Cu^+) at moderate temperatures (room temperature or mild hydro(solvo)-thermal conditions) in the presence of organic template ions. The latter are incorporated into the "holes" and thus determine the "porosity" of the resulting frameworks. This approach let the field expand rapidly and compounds such as $[Et_4N]_2Cu_2Ge_4S_{10}$,[3] $[Me_4N]_2MGe_4S_{10}$ (M = Mn,[4,5] Fe,[5,6] Co,[5] Zn[5]), $[Me_4N]_6(Cu_{0.44}Ge_{0.56}S_{0.73})Ge_4S_{10}$,[7] $[Ph_4P]Hg_2As_4S_9$,[8] $[Me_4N]HgAs_3S_6$,[8] $[Ph_4P]InAs_3S_7$,[9] and $[Me_4N][Rb]BiAs_6S_{12}$[9] were reported. On the other hand, extended structures are also accessible via condensation processes of molecular building blocks with themselves. Several of these "non-functionalized"[10] germanium,[11] tin,[12−19] and antimony sulfides[20,21] have been characterized. In contrast, the use of small alkali cations under similar synthetic conditions gives dense structures with extended inorganic frameworks. Examples include KCu_2AsS_3,[22] KCu_4AsS_4,[22] MAg_2SbS_4,[23] and M_2AgSbS_4[23] (M = Rb, K) as well as $CsSb_2Se_4$,[24] $Rb_2Sn_2Se_5$,[25] $Cs_2Sn_3Se_7$,[26] and $Cs_4Sn_5S_{12}$.[27]

In preceding papers,[8,9] we have demonstrated that the $AsS_3{}^{3-}$ ligand is a powerful building block to form extended structures if it is reacted with metal ions (In^{3+}, Bi^{3+}, Hg^{2+}) in the presence of organic templates. Here we report the interesting two-dimensional material $[Co(en)_3]CoSb_4S_8$ (**1**) which was prepared by heating $CoBr_2$ with Na_3SbS_3[28] and ethylenediamine (en) in H_2O at 130 °C.[29] The green-black compound is insoluble in all common organic solvents.

$[Co(en)_3]CoSb_4S_8$ consists of isolated $[Co(en)_3]^{2+}$ cations and "porous" non-centrosymmetric layers of composition ${}^{2}_{\infty}[CoSb_4S_8]^{2-}$.[30] The characteristic feature of these layers is ${}^{1}_{\infty}[SbS_2]^-$chains running along the *a*-direction. The chains are composed of corner-sharing SbS_3 pyramids, see Figure 1A. The terminal sulfur atoms, which are negatively charged, form bis-chelate-type ligands that bind to the Co atoms which thereby connect the $SbS_2{}^-$ chains to give polar $CoSb_4S_8{}^{2-}$ layers. As a result, these layers are composed of small 6-membered $CoSb_2S_3$ rings and large 20-membered $Co_2Sb_8S_{10}$ rings in which the shortest cross-contact between sulfur atoms is 6.74 Å long, see Figure 1B. Above and below these almost rectangular "holes" reside the $[Co(en)_3]^{2+}$ dications which are normal tris-chelate complexes of Co^{2+} ions with ethylenediamine ligands (Co−N 2.13 Å) in either $\Delta(\lambda\lambda\lambda)$ or $\Lambda(\delta\delta\delta)$ conformation.[30] The CH_2 groups of some of the en ligands protrude throught the $Co_2Sb_8S_{10}$ rings.

The Co atoms in this polymeric framework are in the divalent oxidation state and acquire distorted tetrahedral coordination with normal average bond lengths (2.322 Å) and angles (109.5°).[31] The antimony atoms are pyramidal and reveal pseudo-tetrahedral stereochemistries (Sb−S 2.443 Å; S−Sb−S 97.1°).

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(29) $CoBr_2$ (88 mg; 0.4 mmol) and Na_3SbS_3 (92 mg; 0.32 mmol) were mixed and loaded into a Teflon-lined digestion bomb. A mixture of ethylenediamine (0.32 mL; 4.8 mmol) and deoxygenated H_2O (0.88 mL) was added and the bomb closed and exposed to 130 °C for 3 days. The resulting crude product contained dark-green microcrystals of **1** and some black powder which according to powder pattern analysis is a mixture of $NaSbS_2$ and Sb_2S_3. In a subsequent purification step, this crude material was transferred into a vial which was filled with water and sonicated for a few minutes. Most of the black powder was suspended in water which was then decanted leaving behind the desired compound. This procedure was repeated until the water remained clear. Yield: 55 mg (0.053 mmol; 66% based on Sb). The purity of the material was confirmed by comparison of the observed powder pattern with that calculated from the single-crystal data.

(30) Crystal data: $[Co(en)_3]CoSb_4S_8$, monoclinic, $C2$ with $a = 10.482(2)$ Å, $b = 16.134(2)$ Å, $c = 8.614(2)$ Å, $\beta = 109.84(2)°$, V = 1370.5(5) $Å^3$, $Z = 2$, $D_{calc} = 2.524$ g cm^{-3}, and $\mu = 56.9$ cm^{-1}. Single-crystal X-ray diffraction data were collected at 23 °C on a Rigaku AFC-6S four-circle diffractometer (Mo Kα radiation) with $2\theta/\omega$ scans, $4° < 2\theta < 60°$, and 1617 reflections with $F_o{}^2 > 3\sigma(F_o{}^2)$. An empirical absorption correction (based on ψ-scans) was applied to the data. The number of variables were 119, and the final $R/R_w = 3.5/5.6\%$. The other enantiomer gave insignificantly higher residuals ($R/R_w = 3.6/5.6\%$) and thus it remains uncertain which enantiomer was under investigation. Sigma weights were used. The structure was solved with SHELXS-86 and refined with the TEXSAN Structure Analysis Package (Molecular Structure Corporation, 1985) of crystallographic programs.

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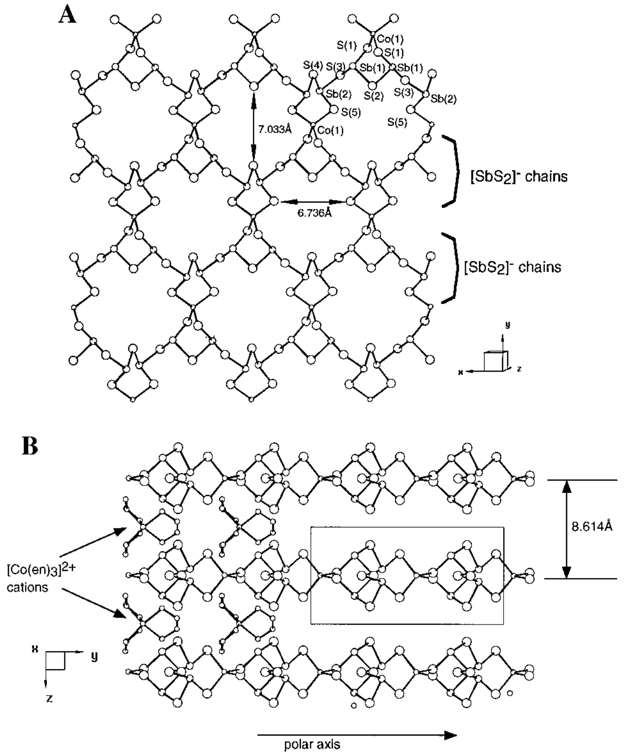

Figure 1. (A) A view of a ${}^{2}_{\infty}[CoSb_4S_8]$ layer. (B) The arrangement of $[Co(en)_3]^{2+}$ cations in the intralamellar space of $[Co(en)_3]CoSb_4S_8$. On the right side of the figure the cations have been omitted to highlight the 8.614 Å high gallery space. The polar axis is along the *b* axis. Selected bond distances (Å) and angles (deg): Sb(1)−S(1) 2.401(4), Sb(1)−S(2) 2.483(4), Sb(1)−S(3) 2.470(4), Sb(2)−S(3) 2.462(4), Sb(2)−S(4) 2.462(5), Sb(2)−S(5) 2.381(4), Co(1)−S(1) 2.322(4), Co(1)−S(5) 2.321(5), S(1)−Sb(1)−S(2) 97.9(1), S(1)−Sb(1)−S(3) 91.4(1), S(2)−Sb(1)−S(3) 98.5(1), S(3)−Sb(2)−S(4) 96.4(1), S(3)−Sb(2)−S(5) 100.2(1), S(4)−Sb(2)−S(5) 98.0(1), S(1)−Co(1)−S(1′) 104.3(2), S(1)−Co(1)−S(5) 112.2(2) (2x), S(1)−Co(1)−S(5) 109.7(1) (2x), S(5)−Co(1)−S(5′) 108.7(2). $[Co(en)_3]^{2+}$ (not depicted): Co(2)−N(1) 2.12(2), Co(2)−N(2) 2.17(2), Co(2)−N(3) 2.11(2); N(1)−Co(2)−N(2) 78.6(7), N(3)−Co(2)−N(3′) 79.9(8).

Magnetic susceptibility measurements on a powdered sample show that the title compound obeys Curie−Weiss law between 100 and 300 K with a Weiss constant of $\Theta = -33$ K. The average effective magnetic moment at room temperature is calculated to be 4.56 μ_B per Co atom. Since the compound contains CoS_4 tetrahedra and CoN_6 octahedra, we were not able to assign the contributions to the magnetic moment of each metal site. Typically, octahedral CoN_6 complexes have magnetic moments between 4.7 and 5.2 μ_B at room temperature, while tetrahedral complexes usually adapt values between 4.4 and 4.8 μ_B.[32] However, the sizable Weiss constant of $\Theta = -33$ K suggests that there are significant antiferromagnetic exchange interactions between the Co atoms in the title compound.

Thermogravimetric analysis shows a clean one-step weight loss of 15.6% at 295 °C which is due to the complete loss of en (ideal: 17.3%). The powder diffraction pattern of the remaining black powder, however, exhibits only peaks of Sb_2S_3. The decomposition product must contain Co/S phases as well, but their composition remains unclear since they are X-ray amorphous.

Attempts to exchange the $[Co(en)_3]^{2+}$ cations with either inorganic or organic cations have been unsuccessful. While aqueous solutions of organic cations such as $[Me_3NH]^+$ and $[Et_3NH]^+$ react with **1** at 130 °C to give Sb_2S_3, from carefully ground and heated (130 °C) mixtures of the title compound with CsI and $[Ni(en)_3]Cl_2$ only the title compound could be recovered. We suppose that the exchange in the latter case is kinetically hindered because of the high Coulomb attractions between the $[Co(en)_3]^{2+}$ dications and the $CoSb_4S_8{}^{2-}$ layers. We anticipate these attractions to be even stronger with tricationic species such as $[Co(en)_3]^{3+}$. In terms of achieving microporosity, a successful exchange with this highly charged complex is even more desirable because it would create more void space between the layers.

This compound is the first example of a transition metal antimony sulfide with a polar anionic porous structure. We expect this to be the first member of a series of compounds of the type $[M(en)_3]M'Sb_4S_8$, where M = Mn, Fe, Co, Ni, Cu and M′ = Mn, Fe, Co, Zn, Cd, Hg, as it was found in the $[Me_4N]MGe_4S_{10}$ series.[4−7] The non-centrosymmetric structure and the possibility for metal substitution suggest that certain members of the family may exhibit good nonlinear optical properties.

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Supporting Information Available: Tables of atomic coordinates and anisotropic thermal parameters of all atoms, bond distances and angles, and positional parameter, *B*(eq), and *U* (9 pages). See any current masthead page for ordering and Internet access instructions.

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