A One-dimensional Germanium Sulfide Polymer Akin to the Ionosilicates: Synthesis and Structural Characterization of DPA-GS-8, $Ge_4S_9(C_3H_7)_2NH_2(C_3H_7)NH_2(C_2H_5)$

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$Ge_4S_9(C_3H_7)_2NH_2(C_3H_7)NH_2(C_2H_5)$ consists of chains of corner-linked adamantane units with a composition of $[Ge_4S_9]^{2-}$ which are separated by two dipropylammonium (DPA) cations; the first reported chain-like structure of $[Ge_4S_9]^{2-}$.

Hydrothermal recrystallization of simple metal oxide and sulfide precursors in the presence of organic amines affords an experimentally straightforward route to microporous materials.[1-3] This method has been successfully employed in the production of aluminosilicate molecular sieves[2,3] and a variety of other oxide frameworks. The most open of these frameworks consist of corner-linked tetrahedral units TO_4 (T = Al, Si) in naturally-occurring zeolite molecular sieves, for example. These materials are composed of a regular array of pores and channels which can be used as molecular sieves, ion exchangers and catalysts. Indeed, the aluminosilicate family of structures[4] is an excellent example of the variety of structure types which are available when tetrahedral centres can be induced to form isolated (nesosilicates such as olivine), 1-connected (sorosilicates such as epidote), 2-connected (ionosilicates such as pyroxene), 3-connected (sheet silicates such as the micas and clays) and 4-connected structures (silicas and zeolites).

More recently, new classes of microporous Sn and Ge sulfides[5-7] were reported. As is usual in the metal chalcogenides, edge-shared structural elements predominate.[8,9] However, the types of connectivity found in the aluminosilicates, where corner-sharing of tetrahedral structural elements is the norm, has been described in some sulfide systems.[10] For the SnOS system,[10,11] tetrahedral clusters of composition $[Sn_{10}S_{20}S_4]^{8-}$ share bridging sulfur atoms to form frameworks akin to the 4-connected networks found in tecto- and phyllo-

silicates.[4] Isolated tetrahedral clusters have also been observed in this system.[12,13]

For the GeS system, examples of structures containing isolated adamantane clusters[14] and dimeric units[13] have been reported. These compounds, $[Me_4N]_4Ge_4S_{10}$ and $Cs_6Ge_8S_{19}·12H_2O$, are composed of isolated $[Ge_4S_{10}]^{4-}$ clusters[14] and dimers in which the $[Ge_4S_9]^{2-}$ units are bridged by a sulfur atom to make a $[Ge_8S_{19}]^{6-}$ ion,[13] respectively; they represent the equivalent of the neso- and soro-silicate group in silicate chemistry.[4] Further condensation of these clusters to form structures reminiscent of the framework silicates has been accomplished by coprecipitation with a metal, e.g. Cu, Zn, Cd and Mn.[5,6,15,16] We report here the first example of a Ge sulfide containing adamantane clusters, $[Ge_4S_9]^{2-}$, linked by bridging sulfurs to form an infinite chain. The linkages in this material, designated DPA-GS-8 by Bedard in the patent describing its synthesis,[5] are reminiscent of those found between tetrahedral elements found in the ionosilicates.[4]

Single crystals of DPA-GS-8 were produced from freshly prepared GeS_2 (0.2 g; 1.46 mmol), 2 mol dm^{-3} dipropylammonium hydrogen chloride (0.4 g; 5.81 mmol), $NaHCO_3$ (0.067 g; 0.80 mmol) and H_2O (0.2 g; 11.1 mmol). Slurries of these starting materials were put in Pyrex-lined bombs and heated at 125 °C under autogenous hydrothermal conditions for 24 h. Yields were greater than 90% based on GeS_2. The positions and intensities of the maxima in the X-ray powder diffraction pattern were very similar for those reported by Bedard[5] for DPA-GS-8.

The structure‡ of DPA-GS-8 (Fig. 1), consists of chains of tetrameric units $[Ge_4S_{10}]^{4-}$ stacked parallel to [100]. A formal oxidation state of +4 was assigned to Ge on the basis of calculations of the bond strength[17] sums from the surrounding sulfurs atoms. The $[Ge_4S_9]^{2-}$ building unit, condensed from
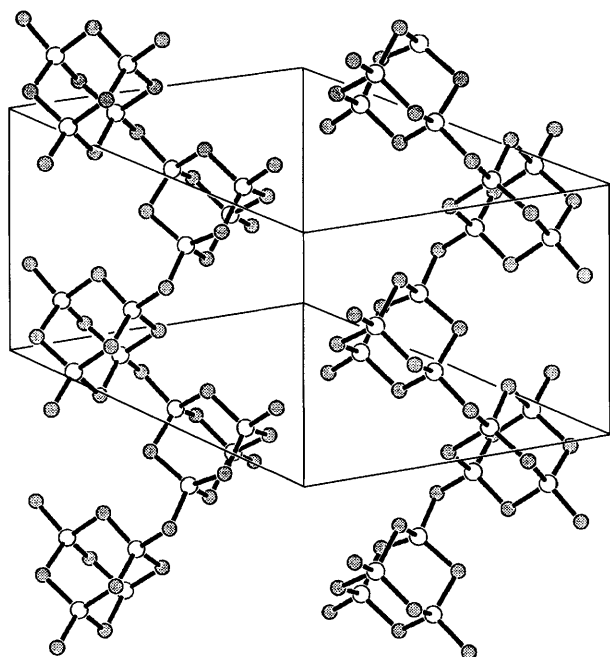

Fig. 1 CHARON§ representation of the chain-like structure of DPA-GS-8. The origin of the unit cell is in the back upper corner, with a to the left, c to the right and b pointing down. Ge atoms in white, S atoms shaded. For the sake of clarity, DPA molecules were omitted.
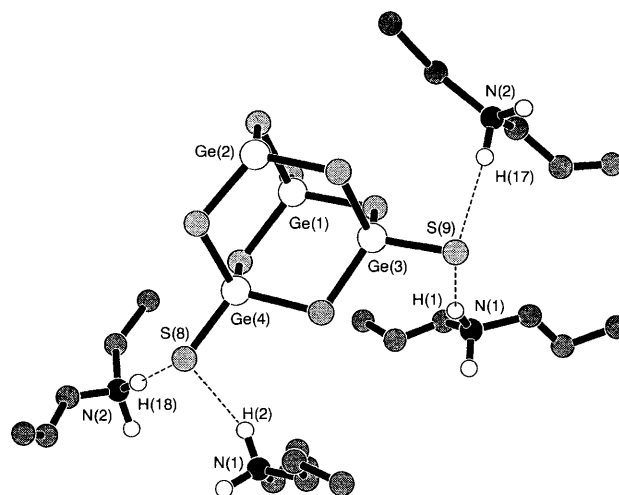

Fig. 2 CHARON§ representation of the hydrogen bonding interaction of $[Ge_4S_9]^{2-}$ with four different DPA cations. Relative bond distances (Å) and angles (°) are: S(8)···H(2) 2.29, S(8)···H(18) 2.47, S(9)···H(1) 2.54, S(9)···H(17) 2.44, H(2)···S(8)···H(18) 99.0, H(1)···S(9)···H(17) 117.9.

four [GeS$_4$]$^{4-}$ primary building units, is similar in geometry to those described in the literature.[8,13,14,18]

The independent chains of [Ge$_4$S$_9$]$^{2-}$ are in a zigzag conformation, reminiscent of the zweier single chains found in the chain silicates.[4] They are isolated from one another by [DPA]$^+$ ions, with the closest Ge–S interchain distance at 5.87 Å, creating a one-dimensional germanium sulfide polymer. A second species, (C$_3$H$_7$)NH$_2$(C$_2$H$_5$) resulting from the decomposition of DPA, is also present between the chains. Decomposition of organic species commonly occurs during hydrothermal treatment,[19,20] and is implicated in the production of more complex networks in these and related systems.[19,20] The close contacts between the calculated hydrogens on the nitrogen of the DPA (Fig. 2) and the terminal sulfurs on the chain, for example S(8)···H(2) 2.29, S(8)···H(18) 2.47, S(9)···H(1) 2.54 and S(9)···H(17) 2.44 Å, are indications that the organic molecule may play a structure directing role.[3,19,21,22] However, since the hydrogens were not located in the structural analysis but calculated, they could be attached to the two terminal sulfurs to produce H$_2$Ge$_4$S$_9$(C$_3$H$_7$)$_2$NH(C$_3$H$_7$)NH(C$_2$H$_5$). The calculated distances for S(8)···N(1) and S(8)···N(2) are 3.25 and 3.50 Å while S(9)···N(1) and S(9)···N(2) are 3.48 and 3.46 Å, respectively.

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Footnotes

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‡ *Crystal data* for DPA-GS-8: Ge$_4$S$_9$(C$_3$H$_7$)$_2$NH$_2$(C$_3$H$_7$)NH$_2$(C$_2$H$_5$), monoclinic, space group *P2$_1$/n, a* = 13.718(2), *b* = 10.7789(9), *c* = 20.350(4) Å, β = 103.382(8)°, *V* = 2925.8 Å^3, *D*$_c$ = 1.742 g cm^{-3}, μ(Mo-Kα) = 46.395 cm^{-1}, *Z* = 4, λ = 0.7107 Å, rectangular crystal, *ca.* 0.07 × 0.10 × 0.15 mm, *R* = 0.050, *R*$_w$ = 0.052, χ^2 = 1.534, for 2262 reflections with *I* > 3σ(*I*). Data collected at 23 °C on an Enraf-Nonius CAD-4 diffractometer and processed using TEXSAN, a suite of programs from Molecular Structure Corporation. DIFABS absorption correction was applied. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ CHARON is a molecular graphics program created by Dr Joseph Lauher at SUNY, StonyBrook.

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