

## Directed Transformation of Molecules to Solids: Synthesis of a Microporous Sulfide from Molecular Germanium Sulfide Cages

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The designed construction of inorganic solid-state materials from distinct and soluble molecular components presents one of the greatest ongoing challenges facing modern synthetic chemistry.<sup>1</sup> Recent attempts to utilize this approach for the preparation of three-dimensional network solids using inorganic molecular precursors have resulted in oligomeric products<sup>2</sup> and noncrystalline materials.<sup>3</sup> The current level of understanding of such chemical syntheses and how to effectively control the atomic structure and the crystallinity of the product is very rudimentary.<sup>4</sup> To investigate and understand the factors affecting such processes, we have begun to examine the chemistry of linking cage structures into three-dimensional networks, using main-group molecular cages as initial objects. We report here the synthesis and structure of an extended microporous sulfide network,  $\text{MnGe}_4\text{S}_{10}\cdot 2(\text{CH}_3)_4\text{N}$ , obtained in crystalline form by the addition copolymerization of Mn(II) with the cage compound,  $\text{Ge}_4\text{S}_{10}[(\text{CH}_3)_4\text{N}]_4$ , at room temperature.

In a digestion bomb,  $\text{GeS}_2$  (0.50 g, 3.7 mmol) and 2 mL of a 2 M aqueous solution of  $(\text{CH}_3)_4\text{NHS}$  were added to 8 mL of an aqueous solution that had been saturated with  $\text{H}_2\text{S}$ . This mixture was heated at 150 °C for 3 days, and the resulting slightly yellowish solution was allowed to stand in an open container. After 24 h, cube-shaped colorless crystals of  $\text{Ge}_4\text{S}_{10}[(\text{CH}_3)_4\text{N}]_4$ <sup>6</sup> were obtained (0.45 g) in 54% yield. This compound is air stable and can be solubilized in water. The tetraethyl- and the tetrapropylammonium salts are prepared similarly, and they are found to have good solubility in most polar organic solvents, such as acetonitrile, *N,N*-dimethylformamide, and 1,2-dichloroethane.

Single crystal structural analysis<sup>7</sup> on  $\text{Ge}_4\text{S}_{10}[(\text{CH}_3)_4\text{N}]_4$  shows the presence of discrete  $(\text{CH}_3)_4\text{N}^+$  cations and  $\text{Ge}_4\text{S}_{10}^{4-}$  anions, which possess an adamantane-like structure, shown in Figure 1.

(1) (a) Mallouk, T. E.; Lee, H. *J. Chem. Educ.* **1990**, *67*, 829–834. (b) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89–112. (c) Whitesides, G. M.; Mathias, J. P.; Seto, C. T. *Science* **1991**, *254*, 1312–1319. (d) Dagai, R. *Chem. Eng. News* **1991**, *69*, 24–30.

(2) For example: (a)  $\text{P}_2\text{W}_{12}\text{O}_{48}\text{H}_4^{10-}$  is condensed to form the tetramer  $\text{P}_8\text{W}_{48}\text{O}_{184}\text{H}_4^{40-}$ ; Contant, R.; Teze, A. *Inorg. Chem.* **1985**, *24*, 4610–4614. (b)  $[\text{Pt}_3(\text{CO})_3(\mu_2\text{-CO})_3]_2^{2-}$  is polymerized to give the pentamer,  $[\text{Pt}_3(\text{CO})_3(\mu_2\text{-CO})_3]_5^{2-}$ ; Calabrese, J. C.; Dahl, L. F.; Chini, P.; Longoni, G.; Matrinenzo, S. *J. Am. Chem. Soc.* **1974**, *96*, 2614–2616. (c)  $[\text{X}]\text{Al}(\text{RSi})_7\text{O}_{12}]^{n-}$  is condensed to make the dimer  $[\text{O}_{12}(\text{RSi})_7\text{AlOAl}(\text{RSi})_7\text{O}_{12}]^{2n-}$  (X = OH, O, OSbMe<sub>3</sub>; R = *c*-C<sub>6</sub>H<sub>11</sub>); Feher, F. J.; Weller, K. J.; Ziller, J. *W. J. Am. Chem. Soc.* **1992**, *114*, 9686–9688.

(3) (a) Day, V. W.; Klemperer, W. G.; Mainz, V. V.; Millar, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 8262–8264. (b) Agaskar, P. A.; Day, V. W.; Klemperer, W. G. *J. Am. Chem. Soc.* **1987**, *109*, 5554–5556.

(4) Stein, A.; Keller, S. W.; Mallouk, T. E. *Science* **1993**, *259*, 1558–1564.

(5) Freshly precipitated crystalline 2.0-g batches of  $\text{GeS}_2$  are obtained from a mixture of an acidified solution of  $\text{GeO}_2$  (1.6 g, 15.4 mmol) and thioacetamide (2.7 g, 35.9 mmol) in water at room temperature.

(6) Anal. Calcd for  $\text{C}_{16}\text{H}_{24}\text{N}_4\text{Ge}_4\text{S}_{10}$ : C, 21.19; H, 5.34; N, 6.17; Ge, 32.02; S, 35.29. Found: C, 21.23; H, 5.44; N, 6.09; Ge, 31.77; S, 35.36.

(7) Single crystals of  $\text{Ge}_4\text{S}_{10}[(\text{CH}_3)_4\text{N}]_4$  were analyzed at 20 °C: cubic, space group  $P4_3m-T_d^4$  (No. 218) with  $a = 19.554(2)$  Å,  $V = 7476(5)$  Å<sup>3</sup>,  $Z = 8$ ,  $d_{\text{calcd}} = 1.613$  g cm<sup>-3</sup>, and  $\mu_a(\text{Mo K}\alpha) = 3.70$  mm<sup>-1</sup>. Data were collected on a Siemens R3m/V autodiffractometer using graphite-monochromated Mo K $\alpha$  radiation and full  $0.8^\circ$  wide  $\theta$  scans to a maximum of  $2\theta = 45^\circ$ , giving 1060 unique reflections. The structure was solved by SHELXTL PLUS direct methods, and the resulting structural parameters were refined by least-squares techniques to a standard discrepancy index  $R = 0.0451$  and  $R_w = 0.0593$  and 776 reflections with  $F > 4\sigma(F)$ . Anisotropic thermal parameters were refined for all non-hydrogen atoms, and fixed thermal parameters were used for included hydrogens.

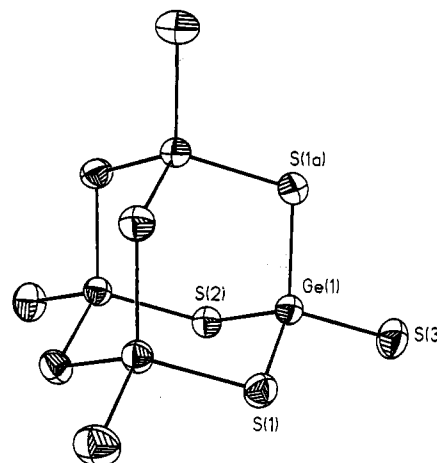


Figure 1. Structure of  $\text{Ge}_4\text{S}_{10}^{4-}$  anion present in crystalline  $\text{Ge}_4\text{S}_{10}\cdot[(\text{CH}_3)_4\text{N}]_4$ , showing 50% probability ellipsoids. The cage has 4 symmetry relating the crystallographically distinct unit to the other three tetrahedral Ge centers.

The tetrahedral anion is composed of four nearly regular tetrahedral Ge(IV) centers, each having one terminal S(3) sulfide and three doubly bridging S(1), S(1a), and S(2) sulfides, where S(1) and S(1a) are symmetry equivalent. Interatomic distances and angles within this anion are essentially coincident with those obtained for  $\text{Ge}_4\text{S}_{10}^{4-}$  cages present in crystals with inorganic cations.<sup>8</sup> The high symmetry and rigidity of this cage coupled to the presence of terminal sulfides as “sticky sites” makes the concept of *directed synthesis* appear viable.

Diffusion of an aqueous solution of  $\text{Mn}(\text{CH}_3\text{CO}_2)_2\cdot 4\text{H}_2\text{O}$  (0.11 g, 0.44 mmol) into another aqueous solution of  $\text{Ge}_4\text{S}_{10}[(\text{CH}_3)_4\text{N}]_4$  (0.20 g, 0.22 mmol) over a 24-h period gives yellow crystals of  $\text{MnGe}_4\text{S}_{10}\cdot 2(\text{CH}_3)_4\text{N}$ <sup>9</sup> in 85% yield.<sup>10</sup> This material is air stable, and it is found to be insoluble in aqueous and nonaqueous media.

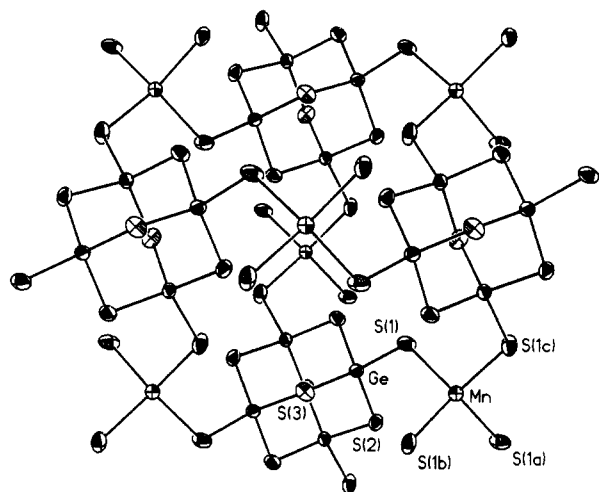
Single crystal structural analysis<sup>11</sup> reveals an extended framework made up of distorted tetrahedral Mn(II) centers, where each center is covalently linked in a three-dimensional arrangement to four terminal sulfides from four independent cages. A truncated portion of the structure is shown in Figure 2; here germanium sulfide cages and Mn(II) ions can be considered as occupying the vertices and edges, respectively, of a tetrahedron, leading to the formation of a larger adamantane-like unit containing large voids. No appreciable change in the interatomic distances and angles within the germanium sulfide building units is observed upon their polymerization. However, the manganese tetrahedral geometry is significantly distorted as a result of binding three cages into a ring motif. The units shown in Figure 2 are

(8) For example: (a)  $\text{Tl}_4\text{Ge}_4\text{S}_{10}$ ; Eulenberger, G. *Acta Crystallogr.* **1976**, *B32*, 3059–3063. (b)  $\text{Cs}_4\text{Ge}_4\text{S}_{10}\cdot 3\text{H}_2\text{O}$ ; Phol, S.; Krebs, B. *Z. Anorg. Allg. Chem.* **1976**, *424*, 265–272. (c)  $\text{Ba}_2\text{Ge}_4\text{S}_{10}$ ; Ribs, M.; Olivier-Fourcade, J.; Philippot, E.; Maurin, M. *J. Solid State Chem.* **1973**, *8*, 195–205. (d)  $\text{Na}_4\text{Ge}_4\text{S}_{10}$ ; Philippot, E.; Ribs, M.; Lindqvist, O. *Rev. Chim. Miner.* **1971**, *8*, 477–489.

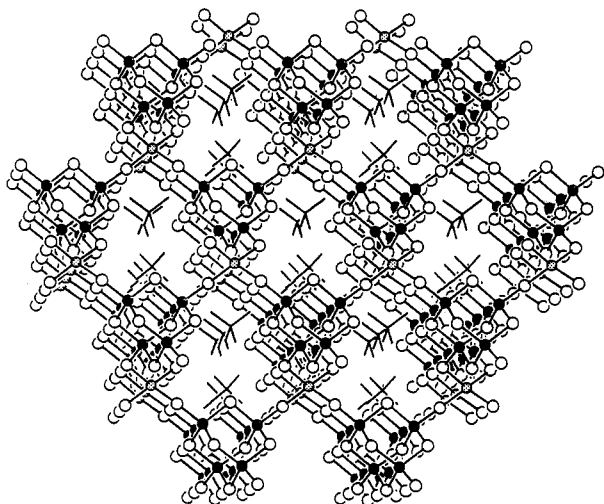
(9) Anal. Calcd for  $\text{C}_8\text{H}_{24}\text{N}_2\text{MnGe}_4\text{S}_{10}$ : C, 11.81; H, 2.97; N, 3.44; Mn, 6.70; Ge, 35.69; S, 39.33. Found: C, 11.83; H, 3.04; N, 3.40; Mn, 6.80; Ge, 35.82; S, 39.20.

(10) The homogeneity of the bulk product was confirmed by comparison of the observed and calculated X-ray powder diffraction patterns. The calculated pattern was produced using the SHELXTL-XPOW program with the single crystal data.<sup>11</sup>

(11) Single crystals of  $\text{MnGe}_4\text{S}_{10}\cdot 2(\text{CH}_3)_4\text{N}$  were analyzed at 20 °C: tetragonal, space group  $I4-S_4^2$  (No. 82) with  $a = 9.513(1)$  Å,  $c = 14.281(2)$  Å,  $V = 1292.4(3)$  Å<sup>3</sup>,  $Z = 2$ ,  $d_{\text{calcd}} = 2.092$  g cm<sup>-3</sup> and  $\mu_a(\text{Mo K}\alpha) = 16.697$  mm<sup>-1</sup>. Data were collected on a Nicolet P1 autodiffractometer using Cu K $\alpha$  radiation and full  $2^\circ$ -wide  $\theta - 2\theta$  scans to a maximum of  $2\theta = 120^\circ$ . The structure was solved by SHELXTL PLUS direct methods, and the resulting structural parameters were refined by least-squares techniques to a standard discrepancy index  $R = 0.0514$  and  $R_w = 0.0666$  for 520 reflections with  $F > 4\sigma(F)$  of 568 independent reflections. Anisotropic thermal parameters were refined for all non-hydrogen atoms, and fixed thermal parameters were used for included hydrogens.



**Figure 2.** Perspective plot using 50% probability ellipsoids of a fragment of the microporous  $\text{MnGe}_4\text{S}_{10}\cdot 2(\text{CH}_3)_4\text{N}$ , showing the aggregation of molecular cages with manganese to form large adamantane-like units. The terminal sulfides present in this fragment are part of other such units making up the overall structure. The asymmetric unit in crystalline  $\text{MnGe}_4\text{S}_{10}\cdot 2(\text{CH}_3)_4\text{N}$  is shown with the atom-labeling scheme; it has 4 symmetry at the Mn center and at the center of the  $\text{Ge}_4\text{S}_{10}$  unit.



**Figure 3.** Structure of  $\text{MnGe}_4\text{S}_{10}\cdot 2(\text{CH}_3)_4\text{N}$  shown approximately down the crystallographic direction [100], which contains  $\text{Ge}_4\text{S}_{10}^{4-}$  anions as building blocks linked by manganese, which is occupying a distorted tetrahedral coordination: dark spheres, Ge; open spheres, S; shaded spheres, Mn. The tunnels thus formed are occupied by  $(\text{CH}_3)_4\text{N}^+$  cations; their carbon core is represented here in a line drawing without the hydrogen atoms for clarity.

then fused together tetrahedrally, resulting in an anionic framework containing a three-dimensional intersecting channel system, where the channels run parallel to the crystallographic directions of [100], [010], and [112]. These channels, shown in Figure 3, are occupied by the tetramethylammonium cations. An alternative way to view this framework is in terms of the diamond

structure, where C has been alternately replaced by  $\text{Ge}_4\text{S}_{10}^{4-}$  cages and Mn(II) centers and C–C by doubly bridging  $\text{S}^{2-}$ . However, unlike the diamond lattice, microporosity is created as a consequence of the larger size of the inorganic cages compared to carbon atoms.<sup>12</sup>

At the outset of this study, reports on microporous sulfides were limited to preliminary studies<sup>13</sup> and some reports which made reference to this class of materials.<sup>14</sup> Given the existence of a wide variety of microporous oxides such as zeolites and their importance in size- and shape-selective reactions, it is worthwhile to consider  $\text{MnGe}_4\text{S}_{10}\cdot 2(\text{CH}_3)_4\text{N}$  as the first in a large class of microporous sulfides. Their chemical characteristics may be as diverse as those associated with  $\beta''$ -alumina<sup>15</sup> solid electrolytes or metal sulfide intercalation systems.<sup>16</sup> Preliminary investigations indicate that the Mn(II) may be replaced by Co(II), Cu(II), Fe(II), and Cd(II) using similar assembly reactions, and the  $(\text{CH}_3)_4\text{N}^+$  cations can be exchanged with metal ions such as  $\text{Hg}^{2+}$ . Thermal gravimetric analysis of this compound showed a weight loss of 15% at 350 °C, corresponding to the decomposition of  $(\text{CH}_3)_4\text{N}^+$  cations, and the integrity of the Mn–Ge–S framework is preserved at this temperature and begins to deteriorate around 500 °C.

The results of the present work have important implications for the use of molecular building blocks in the attainment and the development of directed synthetic routes to useful inorganic solids. Further applications of the synthetic approach described here in the preparation of other microporous phases involving the use of larger organic cations and other molecular building units are currently being explored.

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**Supplementary Material Available:** Crystallographic data for  $\text{Ge}_4\text{S}_{10}[(\text{CH}_3)_4\text{N}]_4$  and  $\text{MnGe}_4\text{S}_{10}\cdot 2(\text{CH}_3)_4\text{N}$ , including crystal structure analysis reports and tables of intensity collections, positional parameters and thermal parameters, and interatomic distances and angles (12 pages); listing of observed and calculated structure factors (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(12) Similarly, see results for  $\text{CuZn}(\text{CN})_4[(\text{CH}_3)_4\text{N}]$  and  $\text{Cu}[\text{C}(\text{C}_6\text{H}_4\text{CN})_4]\text{BF}_4\cdot x\text{C}_6\text{H}_5\text{NO}_2$  coordination solids: Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990**, *112*, 1546–1534. Also see results for the hydrogen-bonded tetrapyrone organic solid: Simard, M.; Su, D.; Wuest, J. D. *J. Am. Chem. Soc.* **1991**, *113*, 4696–4698. These compounds form diamond-like networks.

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