Synthesis and Structure of $MnGe_4S_{10}\cdot(C_6H_{14}N_2)\cdot3H_2O$: A Novel Sulfide Framework Analogous to Zeolite Li-A(BW)

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Single crystals of Dabco−MnGS−SB1 ($MnGe_4S_{10}\cdot(C_6H_{14}N_2)\cdot3H_2O$) were synthesized hydrothermally in the presence of Dabco (1,4-diazabicyclo[2.2.2]octane). This material ($Pna2_1$, $a = 18.367(2)$, $b = 14.184(2)$, and $c = 9.410(1)$ Å) contains $[Ge_4S_{10}]^{4-}$ adamantine clusters corner-linked through distorted Mn^{2+} centers. The alternating Mn^{2+} centers and $[Ge_4S_{10}]^{4-}$ clusters lie at the nodes of a distorted Li-A(BW) net containing elliptical 8-rings. Channels defined by these 8-rings contain the template and water molecules. The distortion of S−Mn−S from the ideal tetrahedral angles is a result of the strain associated with ring system of the framework.

Introduction

Bedard et al.[1] first proposed the synthesis of microporous sulfides possessing structures analogous to those of the oxide molecular sieves. This was based on the observation that a large number of main group and transition elements are known to coordinate tetrahedrally with sulfur, as silicon and aluminum do with oxygen in the aluminosilicates. Using this philosophy, Bedard and several other workers produced a large number of materials[2−15] based upon Ge, Sn, and Sb sulfide chemistry.

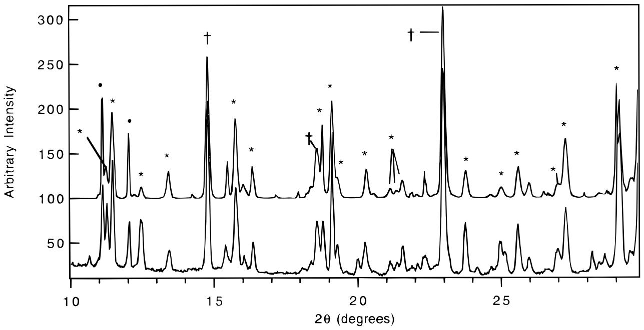

Figure 1. Observed (bottom) and calculated (top) X-ray powder diffraction patterns for the Dabco−MnGS−SB1 sample preparation. Data collection was performed on a Scintag diffractometer using Cu Kα radiation. Peaks marked with asterisks result from the title compound. Major impurity peaks have been labeled as (†) for γ-GeS2 (JCPDS entry 270239) and (●) for the type-3 analogue.[7]

Subsequent crystallographic studies revealed that these materials do not consist of individual corner-linked MS_4 tetrahedra but rather contain corner and edge-linked clusters. Compounds in the Ge−S system are exemplary in this regard. Materials containing isolated adamantine clusters[16] of $[Ge_4S_{10}]^{4-}$ and $[Ge_8S_{19}]^{6-}$ dimers[17] have been described. They represent the structural analogues of the neso- and sorosilicate groups[18] but where the $[SiO_4]^{4-}$ tetrahedron has been replaced by the tetrahedral $[Ge_4S_{10}]^{4-}$ cluster. Infinite chains of $[Ge_4S_{10}]^{4-}$ anions akin to the inosilicate group can be found in DPA-GS-8.[13] Further condensation of these clusters results in structures more reminiscent of the framework silicates. Bedard et al.[1,9] and Parise et al.[19] describe the type-1 structure as a network of four-connected $[Ge_4S_{10}]^{4-}$ clusters resembling the tectosilicate group. Yaghi[7] reports a similar connectivity of both $[Ge_4S_{10}]^{4-}$ clusters and $[MnS_4]^{6-}$ tetrahedra in $MnGe_4S_{10}\cdot2(CH_3)_4N$.

In this publication, we report the synthesis and crystal structure of a novel sulfide compound, $MnGe_4S_{10}\cdot(C_6H_{14}N_2)\cdot3H_2O$, designated Dabco−MnGS−SB1 using the established nomenclature.[9] This compound is comprised of $[Ge_4S_{10}]^{4-}$ adamantine clusters assembled and

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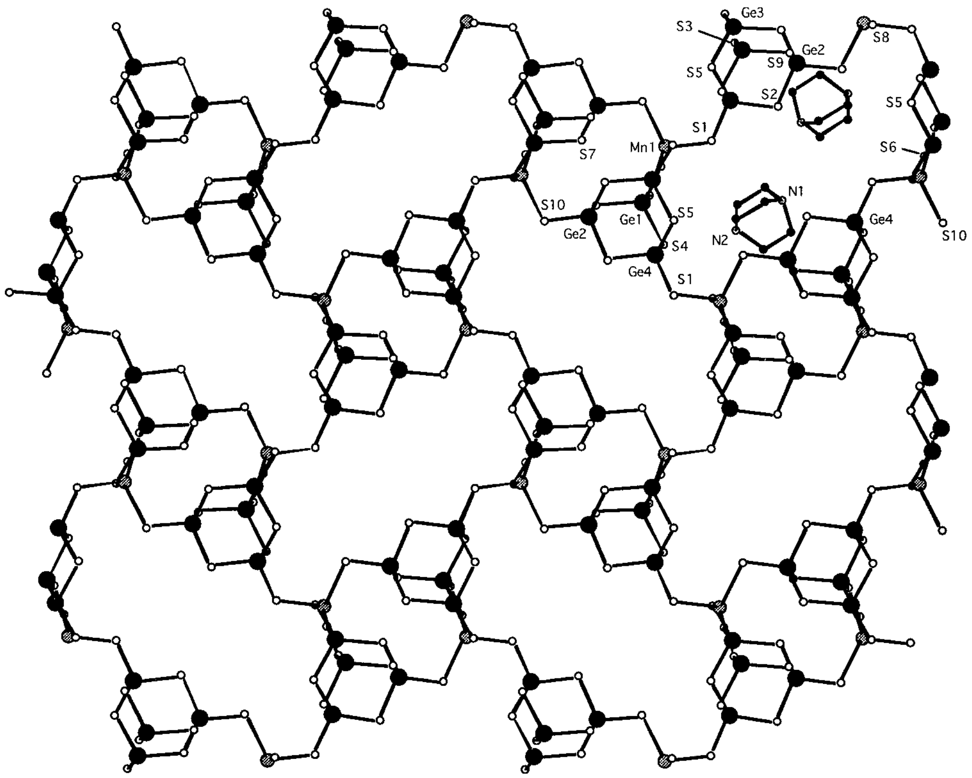

Figure 2. Structure of Dabco−MnGS−SB1 shown along [001]. Unlabeled small black circles are C. The H_2O molecules and hydrogen atoms have been omitted for clarity. Also for clarity, only one channel is shown to contain the Dabco.

linked through Mn^{2+} centers in the presence of the organic templating agent Dabco (1,4-diazabicyclo[2.2.2]-octane).[20] The resulting framework topology is analogous to that of zeolite Li-A(BW)[21] in which the $[AlO_4]^{5-}$ and $[SiO_4]^{4-}$ tetrahedra are replaced by corner-linked $[Ge_4S_{10}]^{4-}$ clusters and $[MnS_4]^{6-}$ tetrahedra.

Experimental Section

Synthesis and Characterization. A mass of 0.196 g of freshly precipitated amorphous GeS_2 was combined with 0.290 g of $MnCl_2{\cdot}4H_2O$, 0.546 g of H_2O, and 0.667 g of 40% Dabco(aq) solution to form a slurry. The Dabco[20] had been saturated with CO_2(g) to aid in solubilizing the GeS_2.[1] The pH of the final mixture was 2.5. The slurry was sealed in Pyrex tubes which were then placed in stainless steel bombs and kept under static conditions and autogenous pressures at 120 °C for 7 days. The product, an off-white powder, was washed with H_2O and EtOH and dried in air. Single crystals 100−200 μm on edge were obtained, and one, 120 × 50 × 50 μm, was isolated for single-crystal X-ray diffraction studies. Qualitative electron probe microanalysis (EPMA) of a single crystal from this batch revealed the presence of Mn, Ge, S, and N.

X-ray Structural Analysis. X-ray powder diffraction data were obtained on a Scintag diffractometer operating in step scan mode and utilizing Cu Kα radiation and a counting time of 25 s for each 0.025° step. The observed and calculated powder patterns are reproduced in Figure 1. Along with the title compound, α-GeS_2 (JCPDS entry 270238),[22] γ-GeS_2 (JCPDS entry 270239), GeS_2 (ICSD entry 31685),[23] GeO_2 (JCPDS entry 361463), and an analogue of the previously reported type-3 structure[7] were observed. Models of the above-mentioned impurity phases were included in the calculated[24] diffraction pattern. The Ge−S phases conceivably recrystallized from the amorphous GeS_2 starting material, whereas GeO_2 is a common impurity in these systems.[6,9]

Single-crystal X-ray precession photographs were indicative of Laue class *mmm* and extinction symbol P*na*. Possible space groups were thus $Pna2_1$ (33) and *Pnam* (62); the former was chosen and confirmed by the subsequent solution and refinement. Data were collected on a Picker four-circle diffractometer as summarized in Table 1. The structure was solved utilizing the direct methods routines in SHELXS-86,[25] with refinements carried out using the least-squares and Fourier routines in the TEXSAN[26] structure analysis software.

Results and Discussion

The Dabco−MnGS−SB1 structure (Figure 2 and Table 2) is an extended framework consisting of distorted tetrahedral Mn^{2+} centers and $[Ge_4S_{10}]^{4-}$ building units. Each of the manganese cations is bound to four terminal sulfur atoms on four different adamantine $[Ge_4S_{10}]^{4-}$ anions creating the familiar "pinwheel arrangement".[1] This connectivity results in large channels that run along [001]. The Dabco and H_2O molecules reside within these channels (Figure 2). Although the hydrogen atoms have not been located, the molecules within the channels are assumed to be protonated to charge balance the anionic framework.

If the $[Ge_4S_{10}]^{4-}$ adamantine units and $[MnS_4]^{6-}$ tetrahedra are represented by nodes placed at the center of the respective cluster, and the bridging sulfur atoms are replaced with straight lines, the framework of zeolite

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[20] Dabco is a registered trademark of Air Products and Chemicals Inc.

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Table 1. Selected Crystallographic Data for $MnGe_4S_{10}[C_6H_{14}N_2]\cdot 3H_2O$

chemical formula	$MnGe_4S_{10}[C_6H_{14}N_2]\cdot 3H_2O$
chemical formula weight	834.18
space group	$Pna2_1$
cell parameters (Å)	$a = 18.367(2)$, $b = 14.184(2)$, $c = 9.410(1)$
volume (Å^3)	2451.43(1)
Z	4
density calcd from formula and cell (g cm^{-3})	2.260
μ(Mo), cm^{-1}	61.006
data collection	Picker diffractometer; $\omega/2\theta$ scans
radiation (graphite monochromator)	Mo Kα
reflections for cell parameters	24 in range $27° < 2\theta < 34°$
measurement temp (K)	295
crystal shape, color, and size	colorless triangular prism, $145 \times 50 \times 50$ μm
max 2θ (deg)	55.2
max h,k,l	23, 18, 11
no. of reflns[a]	3454
data octants	+++, ++−
no. of unique data; $F > 3.0\ \sigma(F)$	2272
merge R for $mm2$	0.053
abs corrn	analytical
refinement method	full-matrix least-squares on F
final R (alternate orientation)	0.0446(0.053)
wR (alternate orientation)	0.0491(0.062)
error of fit, S (alternate orientation)	1.697(2.158)
no. of parameters refined	234
atoms refined	Mn, Ge, N, C, S anisotropic
H positions	calcd, not refined
data/parameter ratio	9.71
weighting scheme	$1/\sigma^2(F)$
max (Δ/σ)	0.00322
max residual electron density (e Å^{-3})	1.738

[a] Three data sets were collected on the same crystal and scaled relative to the first set.

Li-A(BW) emerges[21] (Figure 3). The ABW topology, and thus the Dabco−MnGS−SB1 framework, contains three differently sized rings. A chain of 4-rings comprised of alternating Ge−S clusters and Mn^{2+} atoms zigzags along [001]. 6-rings in the chair conformation stack along [100], while elliptical 8-rings outline the large channels along [001]. As in the 4-rings, the 6- and 8-rings contain an alternating Mn−Ge cluster arrangement (Figure 3).

The ring sizes, determined from the largest distances between sulfur atoms on the Mn^{2+}−Ge^{4+} framework, measure 8.2, 6.8, and 17.2 Å for the 4-, 6-, and 8-rings, respectively. The most notable difference between the structure of Dabco−MnGS−SB1 and that of zeolite Li-A(BW) is the shape of the 8-rings. In Li-A(BW) they are roughly equidimensional, whereas in Dabco−MnGS−SB1 they are elliptical; effectively elongated along [110] or $[\bar{1}10]$. This results in a tilted or staggered packing of the 8-rings (Figure 3). The framework stoichiometry of Dabco−MnGS−SB1 is identical with that of $MnGe_4S_{10}\cdot 2(CH_3)_4N$,[7] Mn:Ge:S = 1:4:10. However, the structures differ in topology (Figure 3); $MnGe_4S_{10}\cdot 2(CH_3)_4N$ is composed only of 6-rings and is analogous to the cristobalite or high-carnegieite structures.

Table 2. Atomic Positional Parameters and B(eq) for Dabco−MnGS−SB1[a]

atom	x	y	z	B(eq)[b]
Ge(1)	−0.12444(8)	−0.3654(1)	0.0930	1.88(6)
Ge(2)	−0.51019(7)	−0.8188(1)	0.3347(2)	1.99(6)
Ge(3)	−0.35210(8)	−0.9409(1)	0.2380(2)	2.10(6)
Ge(4)	−0.34416(7)	−0.69649(9)	0.3199(2)	1.70(6)
Mn(1)	−0.1799(1)	−0.5476(1)	0.3700(3)	2.1(1)
S(1)	−0.2984(2)	−0.5653(2)	0.2520(5)	2.6(2)
S(2)	−0.4632(2)	−0.6777(2)	0.2882(4)	2.3(2)
S(3)	−0.1424(2)	−0.3875(2)	0.3154(4)	2.6(2)
S(4)	−0.1785(2)	−0.2277(2)	0.0492(4)	2.3(2)
S(5)	−0.2967(2)	−0.8075(3)	0.1856(5)	2.9(2)
S(6)	−0.1702(2)	−0.4812(3)	−0.0345(4)	2.7(2)
S(7)	−0.4702(2)	−0.9304(3)	0.1926(5)	2.7(2)
S(8)	−0.1993(2)	−0.5540(3)	0.6257(4)	3.2(2)
S(9)	−0.0053(2)	−0.3555(3)	0.0604(4)	2.8(2)
S(10)	−0.1242(2)	−0.6949(3)	0.2944(5)	2.6(2)
O(1)	−0.1570(7)	−0.907(1)	0.430(2)	5.5(7)
O(2)	0.2348(8)	0.1793(9)	0.910(1)	5.8(7)
O(3)	−0.4014(7)	−0.540(1)	−0.240(2)	6.8(9)
N(1)	−0.3640(8)	−0.278(1)	−0.623(2)	4.5(8)
N(2)	−0.4755(7)	−0.3714(8)	−0.658(2)	3.5(6)
C(1)	−0.432(1)	−0.368(1)	−0.793(2)	3.8(9)
C(2)	−0.363(1)	−0.316(1)	−0.773(2)	5(1)
C(3)	−0.495(1)	−0.275(1)	−0.612(2)	5(1)
C(4)	−0.431(1)	−0.418(1)	−0.547(2)	5(1)
C(5)	−0.427(1)	−0.215(1)	−0.595(2)	5(1)
C(6)	−0.365(1)	−0.359(2)	−0.516(2)	6(1)
H(1)	−0.3193	−0.2424	−0.6077	5.5
H(2)	−0.5189	−0.4085	−0.6741	4.3
H(3)	−0.4221	−0.4312	−0.8234	4.8
H(4)	−0.4606	−0.3378	−0.8647	4.8
H(5)	−0.3581	−0.2647	−0.8397	5.7
H(6)	−0.3211	−0.3566	−0.7870	5.7
H(7)	−0.5275	−0.2454	−0.6824	6.0
H(8)	−0.5222	−0.2760	−0.5245	6.0
H(9)	−0.4591	−0.4237	−0.4608	5.7
H(10)	−0.4166	−0.4793	−0.5760	5.7
H(11)	−0.4248	−0.1885	−0.5018	5.9
H(12)	−0.4273	−0.1632	−0.6621	5.9
H(13)	−0.3207	−0.3965	−0.5256	7.2
H(14)	−0.3652	−0.3348	−0.4209	7.2

[a] Hydrogen positions calculated assuming ideal hydrocarbon geometry. [b] $B_{eq} = {}^{8}/_{3}\pi^2\sum_{i=1}^{3}\sum_{i=1}^{3}U_{ij}a_i^{*}a_j^{*}(\vec{a}_i\cdot\vec{a}_j)$.

Bond lengths (Table 3) within the Mn−S tetrahedron range from 2.433(4) to 2.456(4) Å and are comparable to those in other compounds where Mn^{2+} is tetrahedrally coordinated with S.[7,27,28] Although most S−Mn−S bond angles are close to the ideal expected tetrahedral geometry, those angles within the 4-rings (128.5(2)°) reflect the strain associated with forming this secondary building unit[20] from the tetrahedral centers. The 8-ring contains a strained S10-Mn1-S1 angle (98.7(1)°), while the linkages found in the 6-ring are closer to ideal (Table 3).

The distribution of Ge−S interatomic distances (Table 3) for the GeS_4 tetrahedron is bimodal. Three longer Ge−S bonds that average 2.217 Å involve S atoms bound to two Ge (Figure 2). The Ge−S bonds involving sulfurs bound to Mn^{2+} are shorter and average 2.140 Å, reflecting the underbonding[28] of sulfur coordinated to Mn^{2+} and Ge^{4+} versus two Ge^{4+}. Similar structural systematics can be found in other frameworks consisting of $[Ge_4S_{10}]^{4-}$ adamantine clusters.[1,6,7,10,14,30]

The distances between sulfur atoms on the framework and the nitrogen atoms in the Dabco are 4.1 Å or greater, indicating that hydrogen bonding between template and framework atoms is weak (Figure 3 and Table 2). However, distances between the oxygen atoms in the occluded water molecules and the nitrogen atoms

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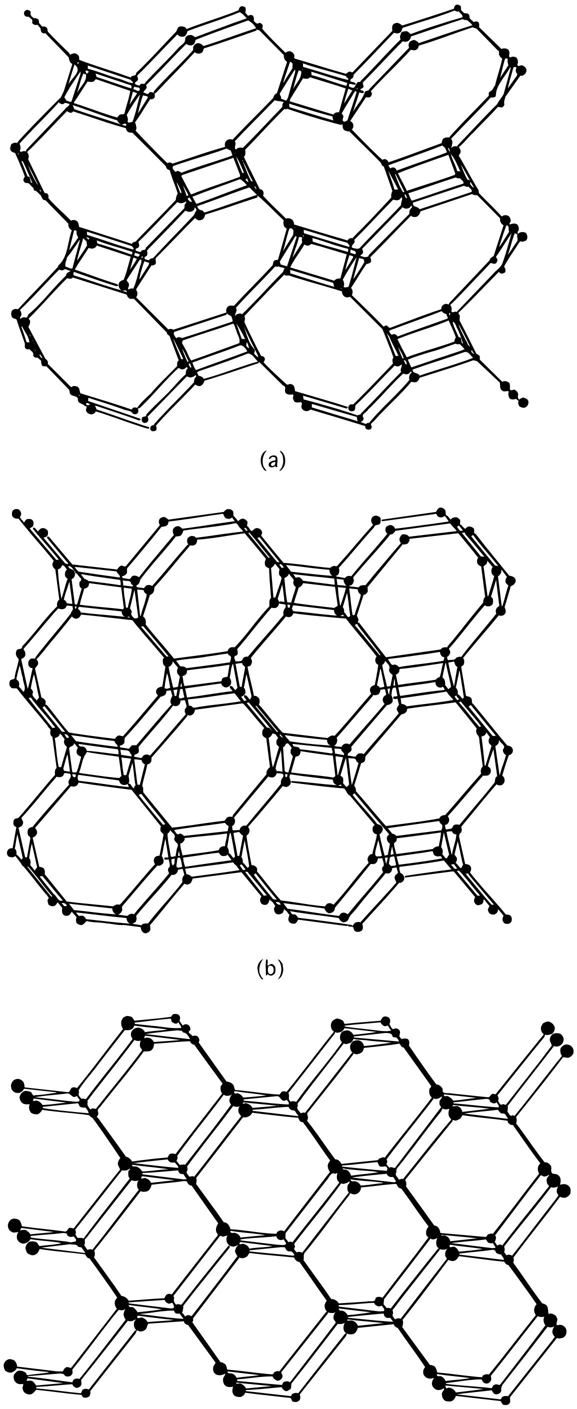
(a)

(b)

(c)

Figure 3. Frameworks of (a) Dabco−MnGS−SB1, (b) zeolite Li-A(BW), and (c) MnGe$_4$S$_{10}$·2(CH$_3$)$_4$N.[7] For the sulfides, each node on the net represents the center of a [Ge$_4$S$_{10}$]$^{4-}$ adamantine unit or the position of a Mn^{2+}. For zeolite Li-A(BW), the nodes represent the positions of Si (Al) atoms. The bridging oxygen (sulfur) atoms are replaced by straight lines to emphasize the framework topology. View for the ABW structure types is along [001]; [100] for MnGe$_4$S$_{10}$·2(CH$_3$)$_4$N.

on the template are as short as 2.7 Å and are indicative of hydrogen bonding (Table 2). These oxygen atoms are also within 3.5 Å of three sulfur atoms on the framework. This situation is similar to that in Dabco−AgGS−SB2, a chain structure consisting of edge-linked 4-rings.[14] In both cases, the Dabco−water component forms a hydrogen-bonded cluster that is in turn bound to the framework portion of the structure. The disposition of the Dabco is indicative of a templating relationship; however, the presence of at least two frameworks within the preparation implies a space-filling role.[31]

Table 3. Selected Interatomic Distances (Å) and Angles (deg) in Dabco−MnGS−SB1

Ge1−S3	2.141(4)	S6−Ge3−S8	101.5(1)
Ge1−S4	2.229(4)	S7−Ge3−S8	112.7(2)
Ge1−S6	2.200(4)	S1−Ge4−S2	104.0(1)
Ge1−S9	2.214(4)	S1−Ge4−S4	112.8(2)
Ge2−S2	2.223(4)	S1−Ge4−S5	107.2(2)
Ge2−S7	2.198(4)	S2−Ge4−S4	109.6(2)
Ge2−S9$^{(a)}$	2.205(4)	S2−Ge4−S5	113.5(2)
Ge2−S10$^{(b)}$	2.138(4)	S4−Ge4−S5	109.8(2)
Ge3−S5	2.204(4)	S1−Mn1−S3	104.6(1)
Ge3−S6$^{(a)}$	2.253(4)	S1−Mn1−S8	108.3(2)
Ge3−S7	2.216(4)	S1−Mn1−S10	98.7(1)
Ge3−S8$^{(c)}$	2.142(4)	S3−Mn1−S8	106.6(2)
Ge4−S1	2.139(4)	S3 −Mn1 −S10	128.5(2)
Ge4−S2	2.223(4)	S8−Mn1−S10	108.6(2)
Ge4−S4$^{(a)}$	2.242(4)	Ge4−S1 −Mn1	107.6(2)
Ge4−S5	2.198(4)	Ge2−S2−Ge4	104.3(1)
Mn1−S1	2.456(4)	Ge1−S3−Mn1	112.8(2)
Mn1−S3	2.428(4)	Ge1−S4 −Ge4	105.6(2)
Mn1−S8	2.434(4)	Ge3−S5 −Ge4	107.7(2)
Mn1−S10	2.433(4)	Ge1−S6−Ge3	105.0(2)
N1 − C2	1.51(3)	Ge2−S7−Ge3	104.9(2)
N1 − C5	1.49(2)	Ge3−S8−Mn1	113.3(2)
N1 − C6	1.52(3)	Ge1−S9−Ge2	106.0(2)
N2 − C1	1.49(2)	Ge2−S10−Mn1	106.4(2)
N2 − C3	1.49(2)	C2 −N1−C5	113(1)
N2 − C4	1.49(2)	C2 −N1−C6	111(1)
C1 − C2	1.49(3)	C5 −N1−C6	109(2)
C3 − C5	1.53(3)	C1 −N2−C3	110(1)
C4 − C6	1.49(3)	C1 −N2−C4	109(1)
S3−Ge1−S4	103.9(2)	C3 −N2−C4	110(1)
S3−Ge1−S6	111.4(2)	N2 −C1−C2	112(1)
S3−Ge1−S9	107.3(2)	N1 −C2−C1	106(2)
S4−Ge1−S6	112.5(2)	N2 −C3−C5	110(1)
S4−Ge1−S9	111.0(2)	N2 −C4−C6	110(2)
S6−Ge1−S9	110.4(2)	N1 −C5−C3	106(1)
S2−Ge2−S7	113.5(2)	N1 −C6−C4	108(2)
S2−Ge2−S9	110.6(1)		
S2−Ge2−S10	105.3(1)	interatomic nonbonding distances (Å)^a	
S7−Ge2−S9	111.9(2)		
S7−Ge2−S10	106.5(2)	S1···O2$^{(d)}$	3.65(1)
S9−Ge2−S10	108.6(2)	S8···O2$^{(e)}$	3.43(1)
S5−Ge3−S6	110.3(2)	S5··· O2$^{(d)}$	3.22(1)
S5−Ge3−S7	110.6(2)	O2··· N1$^{(f)}$	2.78(2)
S5−Ge3−S8	109.3(2)	O3···N2$^{(g)}$	2.69(2)
S6−Ge3−S7	112.2(2)	O1···O3$^{(a)}$	2.70(2)
		S6···O1$^{(h)}$	3.36(1)

[a] Symmetry operators: (a) $-1/2 - x, y - 1/2, 1/2 + z$; (b) $x - 1/2, -3/2 - y, z$; (c) $-1/2 - x, y - 1/2, z - 1/2$; (d) $x - 1/2, -1/2 - y, z - 1$; (e) $x - 1/2, -1/2 - y, z$; (f) $-x, -y, 3/2 + z$; (g) $-1 - x, -1 - y, 1/2 + z$; (h) $-1/2 - x, 1/2 + y, -1/2 + z$.

The formation of Dabco−MnGS−SB1 requires a reaction mixture of lower initial pH than for that of other compounds in the organic−M−GeS system. Bedard et al.[1,9] describe their reaction slurries as having starting pH values of 7−9. The initial pH of the slurry that produces the title compound is 2.5. As mentioned previously, the X-ray powder diffraction data indicates a type-3 analogue structure is present in the product mixture. It is conceivable that this phase forms later as the pH of the reaction mixture changes.

Dabco−MnGS−SB1 represents the first sulfide with a framework topology analogous to that of a zeolite. The observation of 4-, 6-, and 8-rings consisting of alternating Mn-centered and clusters of 4 [GeS$_4$]$^{4-}$ tetrahedra in this structure is also unique in the family of Ge−S materials. The presence of these structural elements and the flexibility of the S−Mn−S connecting angles suggest that larger ring sizes and other zeolite analogues are possible. The variety of structures observed in SiO_2-based frameworks is due in part to the flexibility of the Si−O−Si linkage.[31] In the case of the Ge−S frameworks, the Ge−S−Ge linkage exhibits a more restricted angular range, with only one reported three-dimensional framework without a S−M−S linkage.[1,9,19] Synthetic routes to produce other zeolite analogues may include the use of metals such as Cd,[33] that are capable of more flexible S−M−S linkages.

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Supporting Information Available: Listings of anisotropic thermal parameters, bond distances and angles, intramolecular distances and angles, intermolecular distances and angles, and torsion angles for Dabco−MnGS−SB1 (9 pages); structure factors (8 pages). Ordering information is given on any current masthead page.

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