Inorg. Chem. **2003**, *42*, 7372–7374

Inorganic Chemistry
Communication

Crystal Structure of Thiogermanic Acid $H_4Ge_4S_{10}$

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Received June 12, 2003

X-ray diffraction analysis reveals the thiogermanic acid $H_4Ge_4S_{10}$ possesses discrete adamantane-like $Ge_4S_{10}^{4-}$ complex anions. Each thioanion is composed of four corner shared $GeS_{2.5}^{-}$ tetrahedral units. Crystals were grown from anhydrous liquid hydrogen sulfide reactions with glassy germanium sulfide at room temperature. The crystal structure was solved and refined from single crystal diffractometer data (Mo Kα radiation) obtained at 173 K. $H_4Ge_4S_{10}$ is triclinic, centrosymmetric space group $P\bar{1}$, with $a = 8.621(4)$ Å, $b = 9.899(4)$ Å, $c = 10.009(4)$ Å, $\alpha = 85.963(7)°$, $\beta = 64.714(7)°$, $\gamma = 89.501(8)°$, and $Z = 2$. Average bridging and terminal $\bar{d}$(Ge–S) distances are 2.229 and 2.206 Å, respectively. Vibrational mode assignments are reported from Raman scattering and IR absorption spectra of polycrystalline samples. The ν_s(Ge–S–Ge) and ν_s(Ge–S$^-$) stretching modes are observed at 354 and 405 cm^{-1}, respectively.

Adamantane-like $Ge_4Q_{10}^{4-}$ (Q = S, Se) anions have become increasing popular as building blocks for non-oxide based microstructured materials with open framework topologies resembling those of zeolites.[1−5] These microporous materials may have potential applications as semiconductors (electrocatalysts, photocatalysis, electrochemical sensors), selective absorption membranes, ion exchangers, or electrochemical membranes. Many cations, both inorganic and organic, have been reported to form adamantanoid anions with GeS_2 and $GeSe_2$. Anhydrous inorganic examples include adamantanoid phases of $M_4Ge_4Q_{10}$ (M = Na, K, Rb, Cs, Tl; Q = S, Se) and $Ba_2Ge_4S_{10}$ prepared from solid-state reactions in evacuated silica tubes.[6−12] Recently, we reported an anhydrous $H_4Ge_4S_{10}$ phase from liquid H_2S reactions with quartz-type GeO_2.[13] This phase was previously suggested to have an adamantanoid microstructure from vibrational analysis. In this Communication, the adamantanoid structure is confirmed from X-ray diffraction (XRD) results of single crystals produced from liquid H_2S reactions with glassy GeS_2.

Glassy GeS_2 was prepared by reacting stoichiometric amounts of germanium (Cerac 99.999%) and sulfur (Cerac 99.999%) in an evacuated silica tube. The sealed ampule was rotated horizontally and heated at 1 °C/min to 900 °C inside a tube furnace. After holding for 8 h, the melt was quenched in air and spec milled to a fine powder. Under anhydrous conditions, ~0.5 g of the GeS_2 was reacted with ~7 g of liquid H_2S (Matheson 99.9 mol %, ~0.02 mol % H_2O) at room temperature as described previously.[13] A reaction time of two to four weeks was used to produce single crystals up to 0.8 mm in dimension for the $H_4Ge_4S_{10}$ phase, whereas extended reaction time products (i.e. >eight weeks) were consistent with the low temperature 3D phase of GeS_2 (α-GeS_2). This is in contrast to the reported reactions with GeO_2, where longer reaction times were suggested to produce a dimorphic modification of the $H_4Ge_4S_{10}$ phase in the form of $H_4Ge_4S_{10}.xH_2O$.[13,14] Of the reported inorganic adamantane-like $M_4Ge_4Q_{10}$ phases, only $Na_4Ge_4Se_{10}$ has been previously reported to be dimorphic in nature.[15] In the prepared series, the $H_4Ge_4S_{10}$ and $Na_4Ge_4Se_{10}$ phases have the lowest radius ratios of M to Q suggesting the role of free volume on structural rearrangement. Specifically, the packing of the lower radius ratio systems is more dependent on the anion framework.

Figure 1 is an optical micrograph of a typical cluster of $H_4Ge_4S_{10}$ single crystals. The crystals appear pale with a yellowish tint, nontransparent, prismatic, and non-hydro-

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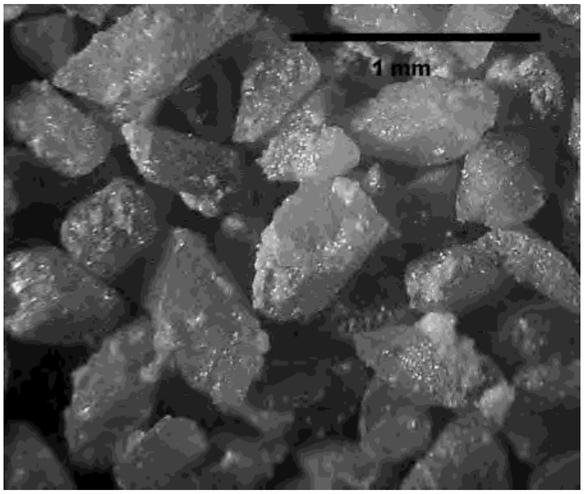

Figure 1. Optical micrograph of a cluster of $H_4Ge_4S_{10}$ prismatic crystals. Single crystals up to 0.8 mm in dimension were grown from anhydrous reactions of glassy GeS_2 with liquid H_2S at room temperature.

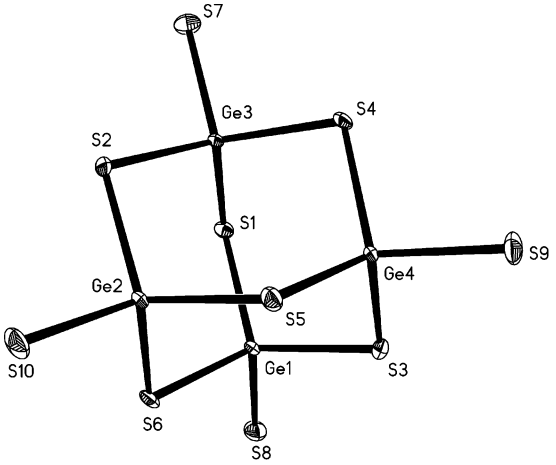

Figure 2. Structural ORTEP drawing of the $Ge_4S_{10}^{4-}$ anion for the thiogermanic acid $H_4Ge_4S_{10}$. Thermal ellipsoids are drawn at the 50% probability level.

Table 1. Bond Lengths (Å) and Angles (deg) for the $Ge_4S_{10}^{4-}$ Anion Present in the $H_4Ge_4S_{10}$ Phase

	Bond Lengths		
Ge(1)−S(8)	2.2025(15)	Ge(3)−S(7)	2.2073(15)
Ge(1)−S(6)	2.2184(15)	Ge(3)−S(2)	2.2252(15)
Ge(1)−S(3)	2.2351(15)	Ge(3)−S(1)	2.2279(14)
Ge(1)−S(1)	2.2372(15)	Ge(3)−S(4)	2.2319(15)
Ge(2)−S(10)	2.2059(16)	Ge(4)−S(9)	2.2080(16)
Ge(2)−S(2)	2.2198(15)	Ge(4)−S(3)	2.2235(14)
Ge(2)−S(6)	2.2295(14)	Ge(4)−S(4)	2.2271(15)
Ge(2)−S(5)	2.2363(15)	Ge(4)−S(5)	2.2301(16)
	Bond Angles		
S(8)−Ge(1)−S(6)	103.83(5)	S(7)−Ge(3)−S(4)	106.06(6)
S(8)−Ge(1)−S(3)	107.07(5)	S(2)−Ge(3)−S(4)	113.57(6)
S(6)−Ge(1)−S(3)	113.45(6)	S(1)−Ge(3)−S(4)	112.28(6)
S(8)−Ge(1)−S(1)	106.88(6)	S(9)−Ge(4)−S(3)	104.85(6)
S(6)−Ge(1)−S(1)	113.43(5)	S(9)−Ge(4)−S(4)	106.18(6)
S(3)−Ge(1)−S(1)	111.46(5)	S(3)−Ge(4)−S(4)	112.29(6)
S(10)−Ge(2)−S(2)	105.01(5)	S(9)−Ge(4)−S(5)	106.71(6)
S(10)−Ge(2)−S(6)	106.66(5)	S(3)−Ge(4)−S(5)	112.98(5)
S(2)−Ge(2)−S(6)	113.12(6)	S(4)−Ge(4)−S(5)	113.07(5)
S(10)−Ge(2)−S(5)	106.65(6)	Ge(3)−S(1)−Ge(1)	102.35(6)
S(2)−Ge(2)−S(5)	113.63(5)	Ge(2)−S(2)−Ge(3)	102.46(5)
S(6)−Ge(2)−S(5)	111.10(5)	Ge(4)−S(3)−Ge(1)	102.13(5)
S(7)−Ge(3)−S(2)	105.93(5)	Ge(4)−S(4)−Ge(3)	102.30(5)
S(7)−Ge(3)−S(1)	105.65(6)	Ge(4)−S(5)−Ge(2)	102.74(6)
S(2)−Ge(3)−S(1)	112.58(5)	Ge(1)−S(6)−Ge(2)	102.58(5)

Table 2. Summary of Crystal Structures for Select Cation Modified Thiogermanates with Adamantane-like $Ge_4S_{10}^{4-}$ Anions

	unit cell	space group	$\bar{d}$ (Ge−S)$_t$ (Å)	$\bar{d}$ (Ge−S)$_b$ (Å)
$H_4Ge_4S_{10}$	triclinic	$P\bar{1}$	2.206	2.229
$Na_4Ge_4S_{10}$[6]	orthorhombic	*Cmcm*	2.139	2.225
$K_4Ge_4S_{10}$[7]	monoclinic	*C*2/*c*	2.115	2.234
$Rb_4Ge_4S_{10}$[7]	monoclinic	*C*2/*c*	2.104	2.220
$Cs_4Ge_4S_{10}$[8]	monoclinic	*C*12/*c*1	2.116	2.239
$Tl_4Ge_4S_{10}$[9]	monoclinic	*C*2/*c*	2.141	2.233
$Ba_2Ge_4S_{10}$[6]	cubic	*Fd*3*m* or *Fd*3	2.192	2.205

scopic in nature. The X-ray single crystal data were collected at 173 K with the hope of resolving the hydrogen positions; unfortunately, they could not be distinguished. The structural data indicated an adamantane-like $Ge_4S_{10}^{4-}$ motif configured in a triclinic unit cell with the centrosymmetric space group $P\bar{1}$.[16] Figure 2 presents a structural representation of the $Ge_4S_{10}^{4-}$ anion for the $H_4Ge_4S_{10}$ phase; Table 1 presents corresponding bond lengths and angles. Table 2 presents a summary of the crystal structure compared to other select cation-modified thiogermanates with adamantanoid microstructures. The mean bridging bond length, $\bar{d}$(Ge−S)$_b$, of 2.229 Å is consistent with those of previously reported adamantanoid thiogermanates, whereas the mean terminal bond length, $\bar{d}$(Ge−S)$_t$, of 2.206 Å is considerably longer than those obtained from adamantanoid units with other monovalent cations. Previously reported mean terminal bond lengths range from 2.104 Å for $Rb_4Ge_4S_{10}$[7] to 2.192 Å for $Ba_2Ge_4S_{10}$.[6] Similar to other adamantanoid phases,[7] the $Ge_4S_{10}^{4-}$ structural unit for the thiogermanic acid phase is not far removed from T_d symmetry despite the adopted space group. Small variations are observed in bond lengths with bridging *d*(Ge−S)$_b$ distances ranging between 2.218 and 2.237 Å and terminal *d*(Ge−S)$_t$ distances ranging between 2.203 and 2.208 Å. Additionally, S−Ge−S bonding angles are close to the ideal tetrahedral value of 109.5° ranging from 103.8° to 113.6°.

Figure 3 presents IR absorption[17] and Raman scattering[18] spectra for polycrystalline samples. The spectra are in good agreement with those previously reported for the $H_4Ge_4S_{10}$ phase using GeO_2 as a precursor.[13] Table 3 presents suggested vibrational mode assignments assuming ideal T_d point group

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(16) The data were collected at 173 K using the full sphere routine with a Bruker CCD-1000 diffractometer with Mo Kα (λ = 0.71073 Å) radiation. Data were corrected for Lorentz and polarization effects as well as absorption during data reduction using SADABS software (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI). The structural refinement method was based on full-matrix least-squares on F^2. Crystal data for $H_4Ge_4S_{10}$: triclinic, $P\bar{1}$; a = 8.621(4) Å, b = 9.899(4) Å, c = 10.009(4) Å, α = 85.963(7)°, β = 64.714(7)°, γ = 89.501(8)°; V = 770.2(6) Å^3; Z = 2; D = 2.652 g/cm^3; μ = 9.048 mm^{-1}; F(000) = 584; R1 = 0.0557, wR2 = 0.1260; and GOF on F^2 is 1.039.

(17) The IR absorption spectrum was collected at 298 K with a Bruker IFS 66v/S spectrometer using 4 cm^{-1} resolution in both the mid-IR and far-IR regions. Pressed CsI powder pellets were prepared using ~1 wt % of sample.

(18) The Raman scattering spectrum was collected at 298 K with a Bruker FT-Raman RFS 100/S spectrometer using a 1064 nm Nd:YAG laser, 2 cm^{-1} resolution, and 300 mW of power focused on ~0.1 mm diameter spot size. Powdered samples were packed into a small aluminum cuplike sample holder and covered with amorphous tape.

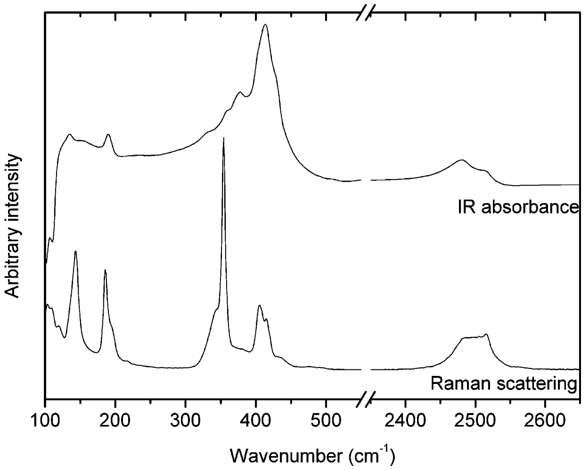

Figure 3. IR and Raman spectra of the thiogermanic acid $H_4Ge_4S_{10}$. A highly symmetric $Ge_4S_{10}^{4-}$ vibrational unit is suggested for this phase. The low-frequency limit of the IR spectrum is limited by the absorption edge of CsI around 140 cm^{-1}.

Table 3. Suggested Vibrational Mode Assignments for the Thiogermanic Acid $H_4Ge_4S_{10}$[a]

	$H_4Ge_4S_{10}$		$Cs_4Ge_4S_{10}$[20]	
	Raman	IR	Raman	IR
ν(S−H)	2484, 2515	2480, 2512		
$\nu_1(A_1)$ {ν_s(Ge−S$^-$)}	405		457	
$\nu_2(A_1)$ {ν_s(Ge−S−Ge)}	354		346	
$\nu_3(A_1)$	186		193	
$\nu_{10}(F_2)$		424	446	455
$\nu_{11}(F_2)$	415	414	405	395
$\nu_{12}(F_2)$		377	378 or 342	372 or 342
$\nu_{13}(F_2)$		190	210	210
$\nu_{14}(F_2)$	144	135	148	148
$\nu_{15}(F_2)$	107	107	112	121

[a] T_d point group symmetry is assumed for the adamantane-like $Ge_4S_{10}^{4-}$ structural unit. Assignments for a comparable reference system are also presented. All units are in wavenumbers (cm^{-1}).

symmetry for the $H_4Ge_4S_{10}$ phase.[19] For the highly symmetric $Ge_4S_{10}^{4-}$ unit, the Raman and IR peaks with the strongest vibrational activity may be attributed to symmetric A_1 and asymmetric F_2 modes, respectively. The symmetric Ge−S−Ge bridging and Ge−S$^-$ terminal stretching modes are assigned at ~354 and ~405 cm^{-1}, respectively. A reduction of local vibrational symmetry was previously suggested from IR activity in the frequency region of the symmetric Ge−S$^-$ terminal stretching mode.[13] However, this remains difficult to resolve because of a strong asymmetric mode at ~414 cm^{-1}. The presence of hydrogen is confirmed by the observance of a S−H stretching mode around 2500 cm^{-1} in both the IR and Raman spectra. Furthermore, two distinct bands in this region suggest two distinct hydrogen environments.

In summary, the crystal structure is reported for the hydrogen thiogermanate $H_4Ge_4S_{10}$. X-ray structural analysis reveals this thiogermanic acid is composed of adamantane-like $Ge_4S_{10}^{4-}$ anions configured in a triclinic unit cell with an adopted space group of $P\bar{1}$. This is consistent with Raman scattering and IR absorption vibrational spectra of polycrystalline samples, suggesting a highly symmetric $Ge_4S_{10}^{4-}$ structural unit terminated by hydrogen.

Acknowledgment. This material is based on the work funded by the United States Department of Energy's Hydrogen Program under Cooperative Agreement DE-FC36-00GO1-531. The authors wish to thank Arkady Ellern with the Chemistry Instrumentation Facility at ISU for the structural solution and refinement task.

Supporting Information Available: Crystallographic file in CIF format for $H_4Ge_4S_{10}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Assuming T_d point symmetry group for the adamantane-like $Ge_4S_{10}^{4-}$ unit, the vibrational modes are distributed among the following Raman (R) and infrared (IR) fundamental vibrations: $\Gamma(T_d) = 3A_1(R) + 3E(R) + 3F_1(\text{inactive}) + 6F_2(\text{IR, R})$.

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