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Preparation and Crystal Structures of Tetrakis(*O*,*O*′-dimethyl dithiophosphato)germanium and Bis[(μ-sulfido)bis(*O*,*O*′-dimethyl dithiophosphato)]digermanium, an Unusual Sulfur-Bridged Binuclear Compound

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In an attempt to prepare tetrakis(*O*,*O*′-dimethyl dithiophosphato)germanium (**1**), $Ge[S_2P(OCH_3)_2]_4$, an unexpected product, bis[(μ-sulfido)bis(*O*,*O*′-dimethyl dithiophosphato)]digermanium (**2**), $[(\mu\text{-}S)Ge[S_2P(OCH_3)_2]_2]_2$, was also obtained. The compounds were characterized by ^1H, ^{13}C, and ^{31}P NMR, IR, and Raman spectroscopy and mass spectrometry. The crystals of both compounds are monoclinic, space group $P2_1/c$. The unit cell dimensions are a = 11.230 (2) Å, b = 23.044 (6) Å, c = 12.086 (3) Å, β = 113.59 (2)°, and Z = 4 for **1** and a = 10.344 (3) Å, b = 12.860 (3) Å, c = 12.443 Å, β = 104.44 (2)°, and Z = 2 for **2**. The dithiophosphate groups are monodentate in both compounds and are arranged in a trans fashion.

Introduction

We recently described the syntheses and NMR, vibrational, and mass spectra of methyl- and phenylgermanium derivatives of dimethyl and diethyl dithiophosphates along with the crystal structures of molecules containing one, two, and three dithiophosphate groups.[1,2] As an extension of this work, we attempted to prepare a fully substituted tetrakis complex using the metathetical reactions of germanium tetrahalides and ammonium dithiophosphate.

$$GeX_4 + 4NH_4S_2P(OCH_3)_2 \rightarrow \underset{\mathbf{1}}{Ge[S_2P(OCH_3)_2]_4} + 4NH_4X$$

However, from $GeCl_4$ only the disubstituted product could be obtained. The use of $GeBr_4$ led to the desired product (**1**) as well as an unexpected product, namely $[(\mu\text{-}S)Ge[S_2P(OCH_3)_2]_2]_2$ (**2**). In this paper, we report the synthesis, spectroscopy, and crystal structures of these two compounds. The structure of compound **1** is the first of a tetrakis compound of this type, while reports of small four-membered GeS rings such as found in compound **2** are relatively rare.[3,4]

Experimental Section

Tetrahalogermanes and the ammonium salt of *O*,*O*′-dimethyl dithiophosphate were purchased from Alfa Inorganics and Aldrich Chemicals, respectively. Carbon disulfide was dried over phosphorus pentoxide prior to distillation. The elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Densities were measured by the flotation method. The melting points were determined on a Fisher-Johns apparatus.

Infrared spectra were recorded on a Nicolet 5DX spectrometer as CsI pellets, and Raman displacements were measured on a Spectra Physics 164 spectrometer using the 5145-Å excitation line of an argon ion laser. ^1H NMR spectra were run in $CDCl_3$ solutions on a Varian EM360 spectrometer (60 MHz) using Me_4Si as internal standard. $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were measured on a Bruker CXP100 FT spectrometer at 22.64 and 36.44 MHz, respectively. $^{13}C\{^1H\}$ NMR chemical shifts were referenced to the central line of the $CDCl_3$ resonance at 77.12 ppm. $^{31}P\{^1H\}$ NMR chemical shifts were referenced to external 85% phosphoric acid. The mass spectra were recorded on a Varian GMAT CH5 spectrometer using the electron impact (EI) mode at 70 eV.

Preparation of Tetrakis(*O*,*O*′-dimethyl dithiophosphato)germanium (1), $Ge[S_2P(OCH_3)_2]_4$. Frozen $GeBr_4$ (0.392 g, 1.0 mmol) was added to dry $NH_4S_2P(OCH_3)_2$ (0.701 g, 4.0 mmol) under nitrogen. After immediate evacuation of the reaction vessel, CS_2 (2 mL) was distilled in. The contents were stirred for 4 h at ambient temperature. The mixture was filtered, and the solvent was evaporated to give a quasi-solid residue. The product was dissolved in fresh CS_2 and recrystallized in the refrigerator. The diamond-shaped colorless crystals were washed with cold *n*-hexane and dried under vacuum: yield 70%; mp 105 °C. Anal. Calcd for $C_8H_{24}S_8P_4O_8Ge$: C, 13.70; H, 3.45. Found: C, 13.33; H, 3.32.

Table I. Summary of Crystal Data, Intensity Collection, and Structural Refinement for $Ge[S_2P(OCH_3)_2]_4$ (**1**) and $[(\mu\text{-}S)Ge[S_2P(OCH_3)_2]_2]_2$ (**2**)

	comp 1	comp 2
formula	$C_8H_{24}S_8P_4O_8Ge$	$C_8H_{24}S_{10}P_4O_8Ge_2$
cell const	11.230 (2), 23.044 (6), 12.086 (3) Å 113.59 (2)°	10.344 (3), 12.860 (3), 12.443 (3) Å 104.44 (2)°
cell volume, Å^3	2866.3 (1)	1602.4 (6)
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
mol wt	700.6	837.2
Z	4	2
d_{calcd}, g cm^{-3}; d_{measd}, g cm^{-3}	1.62; 1.63	1.74; 1.70
cryst dimens, mm	0.18 × 0.19 × 0.37	0.21 × 0.23 × 0.45
abs coeff (μ), cm^{-1}	18.01	26.33
min abs con	1.263	1.69
max abs cor	1.532	2.30
2θ angle, deg	4–45	4–50
radiation	Mo Kα, λ = 0.71069 Å	
monochromator	highly oriented graphite	
temp, °C	21	
scan type	coupled θ (cryst)/2θ (counter)	
scan width, deg	Kα_1 − 1 to Kα_2 + 1	
scan speed, deg min^{-1}	variable, 2.02–4.88	
bkgd time/scan time	0.5	
tot. reflcns measd	4308 (±h,+k,+l)	3302 (±h,+k,+l)
no. of unique data used	2803 [$I > 3\sigma(I)$]	1950 [$I > 3\sigma(I)$]
no. of params	262	145
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.0568	0.0396
$R_w = [\sum w(\|F_o\| - \|F_c\|)^2/\sum w\|F_o\|^2]^{1/2}$	0.0620	0.0432
$\Delta\rho_{max}$, e Å^{-3}	1.3	0.6
shift/error (max)	0.2	0.02

Under similar conditions described for the preparation of compound **1** from $GeBr_4$, reaction of $GeCl_4$ (1 mmol) with $NH_4S_2P(OCH_3)_2$ (4.0 mmol) in CS_2 at 0 °C gave $Cl_2Ge[S_2P(OCH_3)_2]_2$. Anal. Calcd for $C_4H_{12}S_4P_2O_4Cl_2Ge$; C, 10.49; H, 2.64; Cl, 15.49. Found: C, 10.33; H, 2.81; Cl, 15.38. ^1H NMR (in CS_2): 3.79 d ppm (J = 16.2 Hz).

Preparation of Bis[(μ-sulfido)bis(*O*,*O*′-dimethyl dithiophosphato)]digermanium (2), $[(\mu\text{-}S)Ge[S_2P(OCH_3)_2]_2]_2$. Excess $NH_4S_2P(OCH_3)_2$ (0.980 g, 5.6 mmol) was added to a solution of $GeBr_4$ (0.392 g, 1.0 mmol) and CS_2 (5 mL). The mixture was stirred for 5 days under nitrogen at

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(1) Chadha, R. K.; Drake, J. E.; Sarkar, A. B. *Inorg. Chem.* **1985**, *24*, 3156.
(2) Chadha, R. K.; Drake, J. E.; Sarkar, A. B. *J. Organomet. Chem.* **1987**, *323*, 271.
(3) Woinowska, M.; Nollemeyer, M.; Fullgrabe, H. J.; Meller, A. *J. Organomet. Chem.* **1982**, *228*, 229.
(4) Hitchcock, P. B.; Jasim, H. A.; Kelly, R. E.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1985**, 1776.

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Table II. Final Fractional Coordinates and Isotropic Thermal Parameters for Non-Hydrogen Atoms of $Ge[S_2P(OCH_3)_2]_4$ (**1**) with Standard Deviations in Parentheses

	x	y	z	10^3U_{eq},[a] Å^2
Ge	0.22901 (8)	0.11281 (4)	0.26890 (7)	37.7 (5)
S(1)	0.1274 (2)	0.0338 (1)	0.1719 (2)	48 (1)
S(2)	0.3608 (2)	0.0930 (1)	0.4594 (2)	58 (1)
S(3)	0.0937 (2)	0.1850 (1)	0.2633 (2)	54 (1)
S(4)	0.3350 (2)	0.1498 (1)	0.1642 (2)	60 (2)
S(5)	−0.0639 (3)	−0.0629 (2)	0.1986 (3)	101 (3)
S(6)	0.5142 (3)	0.1613 (1)	0.7095 (2)	72 (2)
S(7)	−0.1558 (3)	0.2513 (1)	0.0689 (3)	77 (2)
S(8)	0.4825 (3)	0.0176 (1)	0.2560 (3)	95 (3)
P(1)	0.0609 (2)	−0.0069 (1)	0.2901 (2)	53 (2)
P(2)	−0.3728 (2)	0.1692 (1)	0.5558 (2)	46 (1)
P(3)	−0.0572 (2)	0.1810 (1)	0.0941 (2)	46 (1)
P(4)	0.4890 (2)	0.0920 (1)	0.1925 (2)	52 (2)
O(1)	0.0214 (7)	0.0419 (3)	0.3569 (7)	78 (5)
O(2)	0.1824 (6)	−0.0288 (3)	0.4008 (5)	63 (4)
O(3)	0.3732 (7)	0.2220 (3)	0.4730 (5)	69 (5)
O(4)	0.2345 (6)	0.1826 (3)	0.5534 (6)	63 (4)
O(5)	−0.1282 (6)	0.1234 (3)	0.1010 (5)	66 (4)
O(6)	0.0001 (6)	0.1654 (3)	−0.0007 (5)	63 (4)
O(7)	0.6149 (7)	0.1250 (4)	0.2858 (7)	91 (5)
O(8)	0.5109 (8)	0.0977 (4)	0.0763 (7)	99 (6)
C(1)	−0.1037 (13)	0.0523 (7)	0.3478 (11)	208 (14)
C(2)	0.2641 (12)	−0.0737 (5)	0.3871 (11)	97 (9)

[a] U_{eq} for the non-hydrogen atoms is calculated from the refined anisotropic thermal parameters ($U_{eq} = {}^1/_3\sum_i\sum_jU_{ij}a^*_ia^*_ja_i{\cdot}a_j$).

Table III. Final Fractional Coordinates and Isotropic Thermal Parameters for Non-Hydrogen Atoms of $[(\mu\text{-}S)Ge[S_2P(OCH_3)_2]_2]_2$ (**2**) with Standard Deviations in Parentheses

	x	y	z	10^3U_{eq},[a] Å^2
Ge	−0.00480 (6)	0.03559 (4)	0.11184 (4)	50.0 (3)
S(1)	−0.1009 (2)	0.1823 (1)	0.1460 (1)	68 (1)
S(2)	−0.2775 (2)	−0.0194 (1)	0.2081 (2)	82 (1)
S(3)	0.0878 (2)	−0.0526 (1)	0.2653 (1)	77 (1)
S(4)	0.2520 (2)	0.1754 (2)	0.2735 (1)	92 (1)
S(5)	−0.1361 (2)	−0.0710 (1)	−0.0080 (1)	65 (1)
P(1)	−0.2768 (2)	0.1255 (1)	0.1731 (1)	65 (1)
P(2)	0.2299 (2)	0.0503 (2)	0.3504 (1)	76 (1)
O(1)	−0.3802 (6)	0.1620 (5)	0.0625 (4)	111 (4)
O(2)	−0.3108 (6)	0.2031 (4)	0.2573 (4)	108 (4)
O(3)	0.3554 (6)	−0.0209 (5)	0.3955 (4)	112 (4)
O(4)	0.1997 (8)	0.0628 (5)	0.4675 (4)	128 (5)
C(1)	−0.5144 (9)	0.1538 (8)	0.0431 (8)	141 (8)
C(2)	−0.2635 (13)	0.1965 (9)	0.3709 (6)	171 (10)
C(3)	0.4401 (9)	−0.0479 (8)	0.3275 (9)	145 (9)
C(4)	0.1225 (13)	0.1303 (7)	0.4978 (8)	158 (8)

[a] U_{eq} for the non-hydrogen atoms is calculated from the refined anisotropic thermal parameters ($U_{eq} = {}^1/_3\sum_i\sum_jU_{ij}a^*_ia^*_ja_i{\cdot}a_j$).

Table IV. Interatomic Distances (Å) and Angles (deg) for $Ge[S_2P(OCH_3)_2]_4$

	Distances		
Ge–S(1)	2.218 (2)	P(3)–O(5)	1.568 (7)
Ge–S(2)	2.230 (2)	P(3)–O(6)	1.565 (6)
Ge–S(3)	2.236 (2)	P(4)–O(7)	1.604 (8)
Ge–S(4)	2.224 (3)	P(4)–O(8)	1.526 (8)
S(1)–P(1)	2.081 (3)	O(1)–C(1)	1.39 (1)
S(2)–P(2)	2.080 (3)	O(2)–C(2)	1.44 (1)
S(3)–P(3)	2.071 (3)	O(3)–C(3)	1.41 (1)
S(4)–P(4)	2.100 (3)	O(4)–C(4)	1.44 (1)
S(5)–P(1)	1.900 (4)	O(5)–C(5)	1.43 (1)
S(6)–P(2)	1.909. (3)	O(6)–C(6)	1.42 (1)
S(7)–P(3)	1.917 (3)	O(7)–C(7)	1.40 (1)
S(8)–P(4)	1.890 (4)	O(8)–C(8)	1.46 (1)
P(1)–O(1)	1.550 (7)	Ge···S(5)	5.070
P(1)–O(2)	1.564 (6)	Ge···S(6)	5.120
P(2)–O(3)	1.576 (7)	Ge···S(7)	5.132
P(2)–O(4)	1.573 (7)	Ge···S(8)	3.647
	Angles		
S(1)–Ge–S(2)	111.5 (1)	O(3)–P(2)–O(4)	95.2 (4)
S(1)–Ge–S(3)	113.3 (1)	S(3)–P(3)–S(7)	108.2 (2)
S(2)–Ge–S(3)	110.2 (1)	S(3)–P(3)–O(5)	102.6 (3)
S(1)–Ge–S(4)	107.0 (1)	S(7)–P(3)–O(5)	116.8 (3)
S(2)–Ge–S(4)	112.4 (1)	S(3)–P(3)–O(6)	108.6 (3)
S(3)–Ge–S(4)	102.1 (1)	S(7)–P(3)–O(6)	117.3 (3)
Ge–S(1)–P(1)	104.9 (1)	O(5)–P(3)–O(6)	102.2 (4)
Ge–S(2)–P(2)	105.9 (1)	S(4)–P(4)–S(8)	118.6 (2)
Ge–S(3)–P(3)	105.9 (1)	S(4)–P(4)–O(7)	104.5 (3)
Ge–S(4)–P(4)	104.9 (1)	S(8)–P(4)–O(7)	108.1 (3)
S(1)–P(1)–S(5)	106.9 (2)	S(4)–P(4)–O(8)	102.7 (3)
S(1)–P(1)–O(1)	106.6 (3)	S(8)–P(4)–O(8)	119.9 (4)
S(5)–P(1)–O(1)	119.8 (3)	O(7)–P(4)–O(8)	100.6 (5)
S(1)–P(1)–O(2)	107.6 (3)	P(1)–O(1)–C(1)	125.3 (9)
S(5)–P(1)–O(2)	117.8 (3)	P(1)–O(2)–C(2)	120.8 (6)
O(1)–P(1)–O(2)	97.0 (4)	P(2)–O(3)–C(3)	121.9 (7)
S(2)–P(2)–S(6)	107.9 (1)	P(2)–O(4)–C(4)	119.5 (7)
S(2)–P(2)–O(3)	108.2 (3)	P(3)–O(5)–C(5)	122.1 (6)
S(6)–P(2)–O(3)	118.6 (3)	P(3)–O(6)–C(6)	125.5 (6)
S(2)–P(2)–O(4)	108.2 (3)	P(4)–O(7)–C(7)	124.2 (7)
S(6)–P(2)–O(4)	117.8 (3)	P(4)–O(8)–C(8)	119.2 (8)

[a] Numbers in parentheses refer to estimated standard deviations in the least significant digits.

45 °C before filtration. The filtrate was evaporated under vacuum to give a colorless powder. The product was dissolved in fresh CS_2 and recrystallized in the refrigerator. The colorless square plate crystals thus obtained were washed with cold *n*-hexane and dried: yield 20%; mp 152 °C. Anal. Calcd for $C_8H_{24}S_{10}P_4O_8Ge_2$: C, 11.47; H, 2.89. Found: C, 11.48; H, 2.71.

Alternatively, excess $NH_4S_2P(OCH_3)_2$ (0.860 g, 4.9 mmol) was added to a solution of $GeBr_4$ (0.392 g, 1 mmol), sulfur (0.256 g, 1.0 mmol), and CS_2 (7 mL). The mixture was refluxed for 4 h under nitrogen and filtered. The filtrate was allowed to evaporate in the refrigerator to give crystals of **2**, again in 20% yield based on $GeBr_4$.

Structure Determination and Refinement. Single crystals of suitable dimensions were epoxied to glass fibers and were mounted in arbitrary orientation on a Syntex $P2_1$ diffractometer equipped with a graphite monochromator. The least-squares fit of the angular settings of 15 well-centered reflections ($15 < \theta < 30°$, Mo Kα radiation) yielded the unit cell parameters given in Table I. Systematic absences ($h0l$, l odd; $0k0$, k odd) in structures **1** and **2** uniquely defined the $P2_1/c$ space group. The positions of the Ge atoms were located from sharpened Patterson syntheses, and the remaining atoms were found on subsequent difference Fourier maps. Complete anisotropic refinement minimizing the function $\sum w(|F_o| - |F_c|)^2$ converged at $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.0568$ for **1** or 0.0396 for **2** and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.0620$ for **1** or 0.0432 for **2**, respectively. Hydrogen atoms were included at idealized positions (C–H = 0.95 Å; HCH = 109.5°) with isotropic U's set at 0.01 Å^2 greater than the those for corresponding carbon atoms. A weighting scheme, $w = 1/[\sum\sigma^2(F) + pF^2]$ was used with a final p value of 0.0001 for both compounds. Highest peaks in the final difference Fourier maps were 1.6 e Å^{-3} for **1** and 0.6 e Å^{-3} for **2**, in both cases being around the OCH_3 groups. For compound **1**, data beyond 45° showed unusual decay and were not used. No evidence of secondary extinction was observed for either crystal. Sources of the scattering factors and computer programs have been described previously.[5] The atomic coordinates for non-hydrogen atoms are given in Tables II and III, and important distances and angles are given in Tables IV and V. Additional crystallographic data are available as supplementary material.

Results and Discussion

Compound **1** is formed in 70% yield over a period of a few hours by the simple metathetical reaction (1).

$$GeBr_4 + 4NH_4S_2P(OCH_3)_2 \rightarrow Ge[S_2P(OCH_3)_2]_4 + 4NH_4Br \tag{1}$$

When the reaction is allowed to proceed over an extended number of days, the sulfur-bridged compound **2** is obtained in 20% yield. The production of compound **2** occurs in a matter of hours in the presence of added sulfur. The mechanism of its formation remains obscure because attempts to isolate products other than **2** and NH_4Br resulted in gumlike residues that contained $Br_2Ge[S_2P(OCH_3)_2]_2$ as the only identifiable component. When reaction 1 is carried out with $GeCl_4$ instead of $GeBr_4$, the only germanium-containing product is $Cl_2Ge[S_2P(OCH_3)_2]_2$.

The ORTEP diagram of compound **1** is shown in Figure 1. All of the dithiophosphate groups are monodentate, and as a result

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(5) Chadha, R. K.; Drake, J. E.; Sarkar, A. B. *Inorg. Chem.* **1986**, *25*, 2201.

Table V. Interatomic Distances (Å) and Angles for $[(\mu\text{-}S)Ge[S_2P(OCH_3)_2]_2]_2$ (**2**)[a,b]

Distances			
Ge–S(1)	2.222 (2)	P(2)–O(3)	1.573 (6)
Ge–S(3)	2.223 (2)	P(2)–O(4)	1.573 (5)
Ge–S(5)	2.222 (1)	O(1)–C(1)	1.35 (1)
S(1)–P(1)	2.065 (2)	O(2)–C(2)	1.379 (8)
S(2)–P(1)	1.915 (3)	O(3)–C(3)	1.41 (1)
S(3)–P(2)	2.064 (3)	O(4)–C(4)	1.30 (1)
S(4)–P(2)	1.914 (3)	Ge···S(2)	3.402 (2)
P(1)–O(1)	1.589 (5)	Ge···S(4)	3.417 (2)
P(1)–O(2)	1.548 (5)	Ge···Ge′	2.955 (1)
Angles			
S(1)–Ge–S(3)	112.7 (1)	S(2)–P(1)–O(2)	117.3 (2)
S(1)–Ge–S(5)	115.1 (1)	O(1)[P(1)–O(2)	100.3 (3)
S(3)–Ge–S(5)	108.8 (1)	S(3)–P(2)–S(4)	116.1 (1)
S(5)–Ge–S(5)′	96.7 (1)	S(3)–P(2)–O(3)	103.2 (3)
Ge–S(1)–P(1)	100.7 (1)	S(4)–P(2)–O(3)	118.5 (3)
Ge–S(5)–Ge′	83.3 (1)	S(3)–P(2)–O(4)	105.1 (3)
Ge–S(3)–P(2)	102.3 (1)	S(4)–P(2)–O(4)	117.0 (3)
S(1)–P(1)–S(2)	115.7 (1)	O(3)–P(2)–O(4)	93.8 (3)
S(1)–P(1)–O(1)	100.6 (2)	P(1)–O(1)–C(1)	124.8 (6)
S(2)–P(1)–O(1)	116.4 (3)	P(1)–O(2)–C(2)	124.9 (6)
S(1)–P(1)–O(2)	103.9 (2)	P(2)–O(3)–C(3)	120.8 (6)
		P(2)–O(4)–C(4)	128.4 (8)

[a] Symmetry equivalent position ($-x$, $-y$, $-z$) is denoted by a prime. [b] Numbers in parentheses refer to estimated standard deviations in the least significant digits.

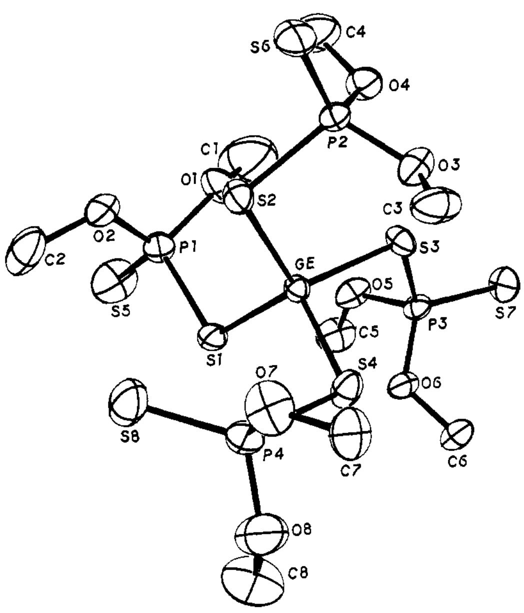

Figure 1. ORTEP drawing of $Ge[S_2P(OCH_3)_2]_4$ (**1**). Atoms are represented by the thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are excluded for clarity.

the germanium atom is bonded to four sulfur atoms. The SGeS angles all vary from the tetrahedral angle in a range between 102.1 (1) and 113.1 (1)°. The average Ge–S bond length is 2.23 Å, which completes a series of measured Ge–S bond lengths of 2.285 (1) Å in $(C_6H_5)_3GeS_2P(OCH_3)_2$,[1] 2.257 (2) and 2.253 (2) Å in $(C_6H_5)_2Ge[S_2P(OCH_3)_2]$,[1] and an average of 2.25 Å in $C_6H_5Ge[S_2P(OCH_3)_2]_3$.[2] The progressive shortening of the Ge–X bond as the more electronegative group, in this case $S_2P(OCH_3)_2$, replaces the less electronegative organo group, in this case C_6H_5, has been noted for simple halide series such as $(CH_3)_nGeX_{4-n'}$ where X = Cl[6] or Br.[7]

In these monodentate ligands, the average P—S(Ge) and P═S bond lengths are 2.08 and 1.90 Å, respectively, which compare well with those found for $(C_6H_5)_3GeS_2P(OCH_3)_2$ of 2.060 (2) and 1.923 (2) and for $(C_6H_5)_2Ge[S_2P(OCH_3)_2]_2$ of 2.04 (average) and 1.90 (average) Å.[1] The nonbonding S atoms appear to be oriented so that they are as far away as possible from the germanium atom thus excluding any possibility of secondary Ge···S interactions. This configuration appears to place the OCH_3 groups into a relatively crowded position with the S—P═S units of the adjacent dithiophosphate groups trans to one another. The divergence from all tetrahedral angles around the phosphorus atoms is relatively large ranging from 119.9 (4)° for an OP═S angle in one group to 95.2 (4)° for the OPO angle in another.

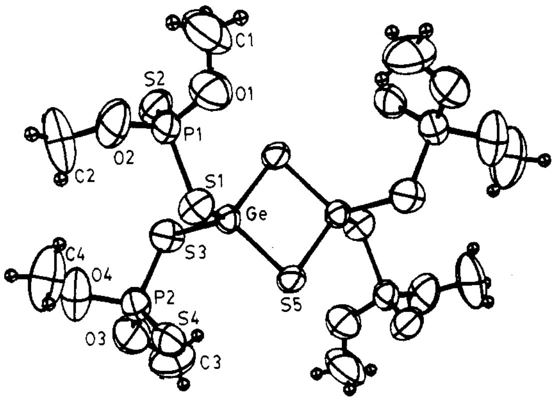

Figure 2. ORTEP drawing of $[(\mu\text{-}S)Ge[S_2P(OCH_3)_2]_2]_2$ (**2**). Atoms are represented by the thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are drawn arbitrarily small for clarity. The halves of the molecule are related by inversion symmetry at the center of the $(\mu\text{-}S)_2Ge_2$ ring.

The ORTEP diagram of compound **2** is shown in Figure 2. Again the dithiophosphate ligands are monodentate, but the difference between P—S(Ge) and P═S bonds lengths, averages of 2.065 and 1.915 Å, respectively, are slightly less marked than in compound **1**. The divergence from all tetrahedral angles about the phosphorus atoms is slightly less marked in compound **2** than in compound **1**, ranging from 118.5 (3)° for an OP═S angle in one dithiophosphate to 100.3 (3)° for the OPO angle in another. The dithiophosphate groups appear to be oriented in a somewhat different fashion because the nonbonding S atoms are now relatively close to germanium, raising the possibility of some Ge···S secondary interactions. The sum of the van der Waals radii for Ge and S is 3.95 Å.[8] In compound **2** the two Ge···S distances are considerably shorter at approximately 3.41 Å. By contrast, in compound **1**, three of the Ge···S distances are close to 5.1 Å while only one is shorter at 3.647 Å. It is possible that the constraints put on the molecule by the formation of the GeS_2Ge bridge system allow for much less stereochemical crowding around germanium so that the terminal S group can be oriented to come closer to germanium.

However, the focus of interest is on the arrangement of the bridging system in which one remarkable feature is that the Ge–S bonds in the bridge, 2.222 (1) Å, have exactly the same bond lengths as those of the terminal Ge–S(P) bonds, 2.222 (2) and 2.223 (2) Å. These bonds are slightly shorter than the corresponding bonds in *cis*-$[(\mu\text{-}S)Ge(CH_2Ph)(NR_2)]_2$, where R = $SiMe_3$,[4] and $[(\mu\text{-}S)Ge(CMe_3)_2]_2$.[3] The $(\mu\text{-}S)_2Ge_2$ unit in compound **2** forms an exact plane ($0.5693x - 0.7757y + 0.2724z = 0$) with crystallographically imposed $\bar{1}$ symmetry. The angles of 83.3 (1)° at sulfur and 96.7 (1)° at germanium are only slightly more distorted from 90° than the corresponding values in $[(\mu\text{-}S)Ge(CMe_3)_2]_2$ of 85.5 (1) and 94.5 (1), respectively.[3]

In general, all of the NMR spectra suggest that the structures of **1** and **2** just described are probably maintained in solution. In Table SI, it can be seen that the ^1H NMR spectra of **1** and **2** confirm that the dithiophosphate groups are also basically linked in identical fashion in both compounds in solution. Thus the OCH_3 peaks appear in both compounds at close to 3.80 ppm as doublets

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(6) Drake, J. E. Hencher, J. L.; Shen, Q. *Can. J. Chem.* **1977**, *55* 1104.

(7) Drake, J. E.; Hemmings, R. T.; Hencher, J. L.; Mustoe, F. M.; Shen, Q. *J. Chem. Soc., Dalton Trans.* **1976**, 822.

(8) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

arising from ^3J(POCH) coupling of 15.5 Hz. Typical values for other dithiophosphates of germanium cover the range 3.33–3.73 ppm with ^3J(POCH) from 14.4 to 16 Hz.[1,2] The OCH_3 chemical shifts in the $^{13}C\{^1H\}$ NMR spectra at 54.77 (**1**) and 54.45 (**2**) ppm also appear as doublets with ^2J(POC) = 5.9 Hz, the former value completing the sequence for $(CH_3)_3Ge[S_2P(OCH_3)_2$, $(CH_3)_2Ge[S_2P(OCH_3)_2]_2$, and $CH_3Ge[S_2P(OCH_3)_2]$ of 53.3, 54.1, and 54.4 ppm, respectively.[1,2] The phosphorus atoms are in almost identical environments with chemical shifts in the $^{31}P\{^1H\}$ NMR spectra of 87.15 and 87.86 ppm respectively for **1** and **2**.

The IR and Raman spectra of the two compounds contain characteristic features that again reflect the similar environments of the dithiophosphate groups (Table SII). In both **1** and **2**, the asymmetric and symmetric $\nu(OCH_3)$ modes can be seen between 1011 and 1044 cm^{-1} and the corresponding $\nu(PO_2)$ modes between 813 and 832 cm^{-1}. The ν(P=S) modes in compound **1** are clearly split and reflect the pseudotetrahedral arrangement. This is particularly evident in the Raman spectra with peaks at 645 and 660 cm^{-1}. In compound **2** there is less splitting with the corresponding peaks in the Raman spectra appearing at 655 and 649 cm^{-1}, the former essentially as a shoulder. Even for the ν(P–S) vibrations of the directly bound sulfur atom, the splitting is larger in the tetrahedral environment of compound **1** than in the bridged system of compound **2**. However, this is hardly surprising as it has been noted for species such as Ga_2Cl_6 that the terminal Ga–Cl modes do not appear to interact to any great extent.[9] The δ(POC) modes in both compounds span the 400–444-cm^{-1} region, while $\delta(PO_2)$ is seen as a typical feature around 330 cm^{-1}. This leaves the Ge–S modes to be assigned in a region where skeletal modes associated with the dithiophosphate group can be identified by comparison with data on series of related species.[10]

It is convenient, in examining the modes associated with the GeS_4 and $S_2Ge(S_2)GeS_2$ skeletons of compounds **1** and **2**, respectively, to draw comparisions with the assignments of $[GaCl_4]^-$ and Ga_2Cl_6, which provide the closest pair of pseudoisoelectronic species. In compound **1**, the four bands associated with the GeS_4 skeleton can be assigned to peaks in the Raman spectrum at 387 and 363 cm^{-1}, the asymmetric and symmetric stretching $\nu(GeS_4)$ modes, and 144 and 117 cm^{-1}, the asymmetric and symmetric deformation $\delta(GeS_4)$ modes. These assignments are close to a set that have been proposed for the $GaCl_4$ modes in $[GaCl_4]^-$ of 380, 346, 153, and 115 cm^{-1}.[11] It seems reasonable to make this comparison rather than the one with $GeCl_4$, where the four vibrations are at 453, 392, 172, and 134 cm^{-1}.[12] The Ge–S bonds are considerably longer (average of 2.23 (1) Å) than the Ge–Cl bonds in $GeCl_4$ (2.112 (1) Å),[13] and the S atom is not strictly terminal so the fundamental vibrations in $GeCl_4$ should be much higher.

There are a total of eight vibrations observed in the Raman spectrum of Ga_2Cl_6,[9] which might be expected to match up reasonably well with the unassigned features in the same region of the spectrum for the Ge_2S_6 skeleton in compound **2**. The features in the spectrum of Ga_2Cl_6 were assigned (cm^1) as 458 m and 405 m, $\nu(GaCl_2$-terminal); ~340 m and 243 m, $\nu(GaCl_2$-ring); 167 m, 125 sh, and 117 w, $\delta(GaCl_2)$; and 98 s, δ(ring mode).[9] The GaCl terminal bond of 2.06 Å is considerably shorter than that of the GaCl ring of 2.29 Å, so the large differences in $\nu(GaCl_2$-terminal) and $\nu(GaCl_2$-ring) are understandable. By contrast, in compound **2**, all four of the Ge–S bonds are of the same length, 2.22 (1) Å, which is similar to the length of the Ga–Cl ring bond. Thus it is reasonable, from the evidence in compound **1**, to expect the GeS_2-terminal modes to be at lower wavenumbers than the terminal modes in Ga_2Cl_6 and the GeS_2-bridging modes to be in regions similar to those in Ga_2Cl_6. The very intense peak at 390 cm^{-1} presumably arises from the accidental degeneracy of a GeS_2-terminal vibration and GeS_2-ring stretching vibration because there is no other obvious explanation for its very high relative intensity. The assignments of the $S_2GeS_2GeS_2$ skeleton then become (cm^{-1}) 399 and 363, $\nu(GeS_2$-terminal); 399 and 244, $\nu(GeS_2$-ring); 160, 144, and 117, $\delta(GeS_2)$; and 82, δ(ring mode). Thus, all of the observed peaks can be assigned in a manner consistent with the observed structures of compounds **1** and **2**.

The mass spectra of the two compounds are summarized in Table SIII. Neither of the compounds gives the molecular ion. The fragmentation patterns differ in the relative intensities although both compounds give identical germanium-containing ions with one exception. In compound **2** the highest observed molecular ion is the one apparently arising from its splitting in half to give $SGe[S_2P(OCH_3)_2]_2^{\bullet+}$. In compound **1**, the highest observed molecular ion is the one arising from the loss of two dithiophosphate groups.

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Registry No. **1**, 109244-70-4; **2**, 109244-68-0; $Cl_2Ge[S_2P(OCH_3)_2]_2$, 109244-69-1.

Supplementary Material Available: Table SI (NMR parameters), Table SII (IR and Raman spectra), Table SIII (mass spectra), Tables SIV and SV (anisotropic thermal parameters for **1** and **2**), Tables SVI and SVII (final fractional coordinates and thermal parameters for hydrogen atoms for **1** and **2**) (8 pages); listings of the observed and calculated structure factors for **1** and **2** (29 pages). Ordering information is given on any current masthead page.

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(9) Beattie, I. R.; Gilson, T.; Cocking, P. *J. Chem. Soc. A* **1967**, 702.

(10) Wafa, O. A.; Lentz, A.; Goubeau, J. *Z. Anorg. Allg. Chem.* **1971**, *380*, 128.

(11) Woodward, L. A.; Garton, G.; Roberts, H. L. *J. Chem. Soc.* **1956**, 3723.

(12) Long, D. A.; Spencer, T. V.; Waters, D. N.; Woodward, L. A. *Proc. R. Soc. London, A* **1957**, *240*, 499.

(13) Morino, Y.; Nakamura, Y.; Tijima, T. *J. Chem. Phys.* **1960**, *32*, 634.