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Preparation, Spectroscopic Characterization, and Crystal Structures of Triphenyl(*O*,*O*′-dimethyl dithiophosphato)germanium and Diphenylbis(*O*,*O*′-dimethyl dithiophosphato)germanium

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$(C_6H_5)_3GeS_2P(OCH_3)_2$ (A) and $(C_6H_5)_2Ge[S_2P(OCH_3)_2]_2$ (B) are prepared from the corresponding phenylchlorogermanes and $NH_4S_2P(OCH_3)_2$. These compounds were characterized by elemental analysis, IR and ^1H, ^{13}C, and ^{31}P NMR spectroscopy, and mass spectrometry. The crystal structure reveals monodentate coordination of the *O*,*O*′-dimethyl dithiophosphate groups and distorted-tetrahedral geometry around the germanium atom. Crystals of A (mp 96 °C) are triclinic, space group $P\bar{1}$, with $Z = 2$, fw = 460.6, $a = 10.311$ (4) Å, $b = 11.282$ (5) Å, $c = 11.517$ (4) Å, $\alpha = 101.47$ (3)°, $\beta = 113.58$ (3)°, $\gamma = 110.31$ (3)° and $V = 1057.5$ (8) Å^3. For 2738 reflections measured at 21 °C with $I > 3\sigma(I)$ (Mo Kα radiation) and 235 parameters, $R = 0.0325$ and $R_{wF} = 0.0353$. Crystals of B (mp 92 °C) are also triclinic, $P\bar{1}$, with $Z = 2$, fw = 540.6, $a = 9.813$ (9) Å, $b = 10.345$ (7) Å, $c = 11.837$ (7) Å, $\alpha = 89.04$ (5)°, $\beta = 85.28$ (6)°, $\gamma = 82.29$ (6)°, and $V = 1186.7$ (16) Å^3. For 2675 reflections with $I > 3\sigma(I)$ and 244 parameters, $R = 0.0581$ and $R_{wF} = 0.0628$.

Introduction

Metallic dithiophosphate esters represent an interesting class of compounds because the group may act in a monodentate fashion as in $Te[S_2P(OCH_3)_2]_2$,[1] fully bidentate as in $Ni[S_2P(OCH_3)_2]_2$,[2] bridging as in $Cu_4[S_2P(OC_3H_7\text{-}i)_2]_4$,[3] and even bridging as well as bidentate as in $Hg[S_2P(OC_3H_7\text{-}i)_2]_2$.[4] Further, the adduct of $Ni[S_2P(OCH_3)_2]_2$ with 2,9-dimethyl-1,10-phenanthroline contains one bidentate and one monodentate ligand.[5] However, in general, it is common to observe bidentate or bridging dithiophosphate groups but relatively rare to find monodentate dithiophosphates. A good deal of information is available concerning lead and tin derivatives,[6-13] but little is known about germanium analogues.[14]

In this paper, we report the synthesis of diphenylbis(*O*,*O*′-dimethyl dithiophosphato)germanium and triphenyl(*O*,*O*′-dimethyl dithiophosphato)germanium along with their characterization by proton, carbon-13, and phosphorus-31 nuclear magnetic resonance spectroscopy, infrared and Raman spectroscopy, and mass spectrometry. In addition, we report their single-crystal structural determinations, which, in both cases, show that the dithiophosphate groups are monodentate and that the compounds are virtually devoid of symmetry.

Experimental Section

Benzene (Fisher ACS) was distilled before use, and carbon disulfide (Fisher ACS) was dried over phosphorus(V) oxide and then distilled. The IR and ^1H NMR spectra of the phenylgermanium chlorides (Alfa) and the ammonium salt of *O*,*O*′-dimethyldithiophosphoric acid (Aldrich) suggested they were sufficiently pure to be used as supplied. The elemental analyses were performed by Guelph Chemical Laboratories, Guelph, Ontario, Canada. Density measurements were performed by the flotation method (C_6H_6/CCl_4). The melting point was recorded on a Fisher-Johns apparatus. The IR spectra were recorded on a Perkin-Elmer 180 double-beam spectrophotometer as Nujol mulls and carbon disulfide solutions on CsI plates. The Raman spectra of solid samples contained in sealed capillaries were measured on a Spectra-Physics 700 Raman spectrophotometer using the 4880-Å exciting line of an argon ion laser. ^1H NMR spectra were recorded on a Varian EM-360 spectrometer in CS_2 using tetramethylsilane as internal standard. $^{13}C\{H\}$ and $^{31}P\{H\}$ NMR spectra were recorded on a Bruker CXP-100 FT spectrometer in $CDCl_3$ solutions. For ^{13}C NMR, the central line of the $CDCl_3$ signal at 77.12 ppm was used as internal standard, while for ^{31}P NMR, 85% phosphoric acid served as external standard (0 ppm). The mass spectra were recorded at 70 eV on a Varian GMAT-CH5 double-focusing mass spectrometer.

Preparation of Triphenyl(*O*,*O*′-dimethyl dithiophosphato)germanium (A), $(C_6H_5)_3GeS_2P(OCH_3)_2$. Benzene (ca. 3 mL) was distilled under vacuum onto a 1:1 mixture of $(C_6H_5)_3GeCl$ and dry $NH_4S_2P(OCH_3)_2$ (typically 2 mmol of each). The mixture was slowly warmed up to ambient temperature and stirred moderately for 3 h. The reaction vessel was occasionally cooled to 0 °C to slow down the reaction and left undisturbed at 0 °C for 12 h. Finally, solid NH_4Cl was filtered, and the filtrate was slowly evaporated under vacuum. The colorless solid product thus obtained was recrystallized from carbon disulfide at 6 °C to give transparent crystals of $(C_6H_5)_3GeS_2P(OCH_3)_2$: yield 70%; mp 96 °C. Anal. Calcd for $C_{20}H_{21}S_2PO_2Ge$: C, 52.10; H, 4.59. Found: C, 52.41; H, 4.70.

Preparation of Diphenylbis(*O*,*O*′-dimethyl dithiophosphato)germanium (B), $(C_6H_5)_2Ge[S_2P(OCH_3)_2]_2$. To the dry $NH_4S_2P(OCH_3)_2$ salt (2 mmol) was added a solution of $(C_6H_5)_2GeCl_2$ (1 mmol) in benzene (3.5 mL) under a nitrogen atmosphere. The mixture was quickly frozen in liquid nitrogen, and the reaction vessel was evacuated on a vacuum line. The reaction mixture was gradually warmed to ambient temperature and stirred continuously for 12 h with occasional cooling to 0 °C. Eventually, the vessel was cooled to 0 °C, and solid NH_4Cl was separated by filtration. The solvent was slowly evaporated, and a white powder formed. The product was dissolved in carbon disuflide and recrystallized at 6 °C to obtain colorless crystals of $(C_6H_5)_2Ge[S_2P(OCH_3)_2]_2$: yield 78%; mp 92 °C. Anal. Calcd for $C_{16}H_{22}O_4P_2S_4Ge$: C, 35.91; H, 4.10. Found: C, 35.24; H, 3.92.

Structure Determination and Refinement. A suitable crystal of A (or B) was sealed in a capillary tube and mounted along the largest dimension on a Syntex P2$_1$ diffractometer equipped with a scintillation counter and a graphite monochromator. The least-squares refinement of the setting angles of 25 high-angle reflections (15° > 2θ > 30°, Mo Kα radiation) yielded the cell dimensions given in Table I. The space group $P\bar{1}$ was used and later assumed correct because of successful refinement of the structures.

Data were collected with use of the $\theta/2\theta$ scan technique; the details of other pertinent X-ray data are given in Table I. The intensities of the three monitor reflections did not change significantly during data collection. The data were corrected for Lorentz and polarization effects, and an analytical absorption correction was applied with use of ABSORB.

The position of the germanium atom was determined by a sharpened Patterson synthesis using SHELX, and subsequent difference maps revealed

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Table I. Crystallographic Data

	$(C_6H_5)_2Ge[S_2P(OCH_3)_2]_2$ (B)	$(C_6H_5)_3GeS_2P(OCH_3)_2$ (A)
a, Å	9.813 (9)	10.311 (4)
b, Å	10.345 (7)	11.282 (5)
c, Å	11.837 (7)	11.517 (4)
α, deg	89.04 (5)	101.47 (3)
β, deg	85.28 (6)	113.68 (3)
γ, deg	82.29 (6)	110.31 (3)
V, Å^3	1186.7 (16)	1057.5 (8)
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
mol wt	540.6	460.6
Z	2	2
ρ_{clcd}, g cm^{-3}	1.51	1.45
ρ_{obsd}, g cm^{-3}	1.52	1.42
cryst dimens, mm	0.12 × 0.23 × 0.38	0.14 × 0.37 × 0.38
radiation	Mo Kα 0.71069 Å	Mo Kα, 0.71069 Å
monochromator	highly oriented graphite	highly oriented graphite
temp, °C	21	21
abs coeff, μ, cm^{-1}	17.07	16.53
min abs corr	1.214	1.225
max abs corr	1.666	1.898
2θ angle, deg	4–50	4–50
scan type	coupled θ(cryst/2θ(counter)	coupled θ(cryst)/2θ(counter)
scan width	Kα_1 − 1° to Kα_2 + 1°	Kα_1 − 1° to Kα_2 + 1°
scan speed, deg min^{-1}	variable, 2.02–4.88	variable, 2.02–4.88
bkgd time/scan time	0.5	0.5
total reflcns measd	4207 ($+h,\pm k,\pm l$)	3748 ($+h,\pm k,\pm l$)
unique data used	2675 [$I > 3\sigma(I)$], R = 0.0	2738 [$I > 3\sigma(I)$], R = 0.0
no. of params (NP)	244	235
R	0.0581	0.0325
R_{wF}	0.0628	0.0353

Table II. Final Fractional Coordinates and Isotropic Thermal Parameters for Non-Hydrogen Atoms of $Ph_3GeS_2P(OMe)_2$ with Standard Deviations in Parentheses

	x	y	z	U_{eq},[a] Å^2 × 10^3
Ge	0.16862 (4)	0.05388 (4)	0.35761 (4)	37.0 (2)
S(1)	0.2754 (1)	0.0791 (1)	0.2189 (1)	45 (1)
S(2)	0.4406 (1)	0.2991 (1)	0.1122 (1)	54 (1)
P	0.3599 (1)	0.2797 (1)	0.2354 (1)	39 (1)
O(1)	0.2252 (3)	0.3235 (2)	0.2164 (2)	45 (2)
O(2)	0.4793 (3)	0.3779 (3)	0.3927 (2)	52 (2)
C(1)	0.0950 (5)	0.2831 (5)	0.0811 (4)	62 (2)
C(2)	0.6359 (5)	0.3917 (5)	0.4655 (5)	76 (3)
C(11)	0.3352 (4)	0.1379 (4)	0.5521 (3)	41 (2)
C(12)	0.3601 (4)	0.0530 (4)	0.6209 (4)	49 (2)
C(13)	0.4709 (5)	0.1089 (5)	0.7604 (4)	74 (3)
C(14)	0.5551 (5)	0.2486 (5)	0.8333 (4)	60 (3)
C(15)	0.5312 (5)	0.3338 (4)	0.7670 (4)	62 (3)
C(16)	0.4215 (5)	0.2794 (4)	0.6270 (4)	52 (2)
C(21)	0.0650 (4)	−0.1455 (3)	0.2923 (3)	43 (2)
C(22)	−0.0945 (5)	−0.2203 (4)	0.2569 (4)	64 (2)
C(23)	−0.1646 (5)	−0.3622 (4)	0.2130 (4)	64 (2)
C(24)	−0.0799 (6)	−0.4303 (4)	0.2033 (4)	68 (3)
C(25)	0.0762 (6)	−0.3581 (4)	0.2354 (4)	67 (3)
C(26)	0.1492 (5)	−0.2170 (4)	0.2801 (4)	54 (2)
C(31)	0.0136 (4)	0.1209 (4)	0.3130 (4)	40 (2)
C(32)	−0.1174 (5)	0.0620 (4)	0.1803 (4)	53 (2)
C(33)	−0.2284 (5)	0.1089 (5)	0.1459 (5)	67 (3)
C(34)	−0.2089 (6)	0.2173 (5)	0.2444 (6)	76 (4)
C(35)	−0.0823 (6)	0.2758 (5)	0.3767 (6)	73 (3)
C(36)	0.0294 (5)	0.2281 (4)	0.4114 (4)	56 (3)

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

Table III. Final Fractional Coordinates and Isotropic Thermal Parameters for Non-Hydrogen Atoms of $Ph_2Ge[S_2P(OMe)_2]_2$ with Standard Deviations in Parentheses

	x	y	z	U_{eq},[a] Å^2 × 10^3
Ge	0.40012 (8)	0.12913 (7)	0.25677 (6)	41.2 (5)
S(1)	0.2902 (2)	0.1033 (2)	0.1002 (2)	61 (1)
S(2)	0.1846 (3)	0.2870 (3)	−0.1109 (2)	82 (2)
S(3)	0.4675 (2)	−0.0772 (2)	0.3127 (2)	59 (1)
S(4)	0.3241 (3)	−0.3346 (2)	0.3979 (2)	74 (2)
P(1)	0.2740 (2)	0.2836 (2)	0.0256 (2)	55 (1)
P(2)	0.2896 (2)	−0.1564 (2)	0.3530 (2)	59 (1)
O(1)	0.1884 (10)	0.3683 (8)	0.1271 (7)	126 (7)
O(2)	0.4049 (7)	0.3474 (7)	0.0243 (6)	91 (5)
O(3)	0.1843 (7)	−0.0668 (6)	0.4285 (7)	96 (5)
O(4)	0.2163 (8)	−0.1339 (7)	0.2358 (6)	109 (6)
C(1)	0.1585 (12)	0.4963 (10)	0.1321 (10)	104 (9)
C(2)	0.5146 (9)	0.3134 (12)	−0.0648 (9)	104 (9)
C(3)	0.2076 (13)	−0.0564 (10)	0.5493 (8)	108 (7)
C(4)	0.0889 (10)	−0.1569 (10)	0.2206 (9)	86 (7)
C(11)	0.2822 (8)	0.2253 (7)	0.3740 (6)	49 (4)
C(12)	0.1406 (8)	0.2459 (8)	0.3723 (7)	62 (5)
C(13)	0.0625 (10)	0.3120 (10)	0.4618 (10)	85 (7)
C(14)	0.1260 (14)	0.3552 (10)	0.5523 (9)	91 (6)
C(15)	0.2669 (13)	0.3347 (10)	0.5520 (8)	88 (8)
C(16)	0.3448 (10)	0.2693 (8)	0.4634 (7)	67 (6)
C(21)	0.5757 (7)	0.1901 (7)	0.2180 (6)	44 (4)
C(22)	0.5931 (9)	0.3181 (8)	0.2411 (7)	62 (5)
C(23)	0.7232 (12)	0.3603 (11)	0.2103 (9)	85 (8)
C(24)	0.8270 (11)	0.2757 (13)	0.1560 (9)	89 (8)
C(25)	0.8092 (9)	0.1507 (11)	0.1312 (8)	80 (7)
C(26)	0.6835 (8)	0.1089 (8)	0.1631 (7)	58 (5)

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

the remaining atoms. Complete anisotropic refinement minimizing the function $\sum w(|F_o| - |F_c|)^2$ converged at $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.0325$ (A) or 0.0581 (B) and $R_{wF} = [\sum w\Delta^2/wF_o^2]^{1/2} = 0.0353$ (A) or 0.0628 (B). Hydrogen atoms were included at the idealized positions (C–H = 0.95 Å, H–C–H = 109.5°) with isotropic U's set at 0.1 Å^2 greater than that of the corresponding carbon atom. A weighting scheme of the form $w = 1/[\sum\sigma^2(F) + pF^2]$ was employed with a final p value of 0.0001 for both A and B. A few peaks of the order of 1.2 e Å^{-3} were found in the final difference maps of B around the methoxy groups O(2)C(2) and O(4)C(4) of the dithiophosphate ligands, suggesting some disorder. The maximum peak in the final difference map of B was 0.6 e Å^{-3}. However, in the last cycle no parameter changed by more than 0.1σ. No evidence of secondary extinction was found.

Sources of the scattering factors and computer programs are given elsewhere.[15] The final atomic coordinates for non-hydrogen atoms are

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Table IV. Interatomic Distances (Å) and Angles (deg) for $(C_6H_5)_3GeS_2P(OCH_3)_2$

Ge–S(1)	2.285 (1)	Ge- - -S(2)′	5.253 (1)
Ge–C(11)	1.950 (5)	ring C(11)–C(16)	
Ge–C(21)	1.944 (5)	mean C–C	1.380 (8)[a]
Ge–C(31)	1.930 (5)	mean C–C–C	120.0 (5)
S(1)–P	2.060 (2)	ring C(21)–C(26)	
S(2)–P	1.923 (2)	mean C–C	1.383 (9)
P–O(1)	1.580 (3)	mean C–C–C	120.0 (6)
P–O(2)	1.578 (3)	ring C(31)–C(36)	
O(1)–C(1)	1.433 (6)	mean C–C	1.381 (9)
O(2)–C(2)	1.421 (6)	mean C–C–C	120.0 (6)

S(1)–Ge–C(11)	111.9 (1)	S(2)–P–O(2)	117.2 (2)
S(1)–Ge–C(21)	98.7 (1)	O(1)–P–O(2)	95.7 (2)
S(1)–Ge–C(31)	108.3 (1)	P–O(1)–C(1)	120.2 (3)
C(11)–Ge–C(21)	110.6 (2)	P–O(2)–C(2)	121.2 (4)
C(11)–Ge–C(31)	114.4 (2)	Ge–C(11)–C(12)	118.6 (4)
C(21)–Ge–C(31)	111.8 (2)	Ge–C(11)–C(16)	122.6 (4)
Ge–S(1)–P	109.0 (1)	Ge–C(21)–C(22)	120.7 (4)
S(1)–P–S(2)	109.1 (1)	Ge–C(21)–C(26)	120.7 (4)
S(1)–P–O(1)	109.2 (1)	Ge–C(31)–C(32)	119.8 (4)
S(2)–P–O(1)	116.3 (1)	Ge–C(31)–C(36)	121.7 (4)
S(1)–P–O(2)	108.6 (1)		

[a] Esd's on mean values have been calculated with the use of the scatter formula $\sigma = [\sum(d_i - \bar{d})^2/(N-1)]^{1/2}$, where d_i is the *i*th and $\bar{d}$ is the mean of *N* equal measurements.

Table V. Interatomic Distances (Å) and Angles (deg) for $(C_6H_5)_2Ge[S_2P(OCH_3)_2]_2$

Ge–S(1)	2.257 (2)	O(1)–C(1)	1.319 (11)
Ge–S(3)	2.253 (2)	O(2)–C(2)	1.455 (10)
Ge–C(11)	1.931 (7)	O(3)–C(3)	1.475 (10)
Ge–C(21)	1.931 (7)	O(4)–C(4)	1.330 (10)
S(1)–P(1)	2.043 (3)	ring C(11)–C(16)	
S(2)–P(1)	1.898 (3)	mean C–C	1.381 (12)[a]
S(3)–P(2)	2.045 (3)	mean C–C–C	120.0 (9)
S(4)–P(2)	1.904 (3)	ring C(21)–C(26)	
P(1)–O(1)	1.609 (8)	mean C–C	1.387 (12)
P(1)–O(2)	1.520 (6)	mean C–C–C	120.0 (8)
P(2)–O(3)	1.530 (7)	Ge- - -S(3)′	5.363 (2)
P(2)–O(4)	1.614 (7)	Ge- - -S(1)′	5.398 (2)

S(1)–Ge–S(3)	103.4 (1)	S(3)–P(2)–S(4)	112.4 (1)
S(1)–Ge–C(11)	112.7 (2)	S(3)–P(2)–O(3)	112.4 (3)
S(3)–Ge–C(11)	111.3 (2)	S(4)–P(2)–O(3)	117.1 (3)
S(1)–Ge–C(21)	111.1 (2)	S(3)–P(2)–O(4)	100.8 (3)
S(3)–Ge–C(21)	101.3 (2)	S(4)–P(2)–O(4)	113.9 (3)
C(11)–Ge–C(21)	115.8 (3)	O(3)–P(2)–O(4)	98.3 (4)
Ge–S(1)–P(1)	103.7 (1)	P(1)–O(1)–C(1)	127.4 (8)
Ge–S(3)–P(2)	105.6 (1)	P(1)–O(2)–C(2)	119.1 (6)
S(1)–P(1)–S(2)	111.9 (1)	P(2)–O(3)–C(3)	118.4 (7)
S(1)–P(1)–O(1)	99.6 (3)	P(2)–O(4)–C(4)	125.2 (7)
S(2)–P(1)–O(1)	114.7 (4)	Ge–C(11)–C(12)	122.2 (6)
S(1)–P(1)–O(2)	113.6 (3)	Ge–C(11)–C(16)	117.3 (6)
S(2)–P(1)–O(2)	117.6 (3)	Ge–C(21)–C(22)	120.1 (6)
O(1)–P(1)–O(2)	97.1 (5)	Ge–C(21)–C(26)	120.5 (6)

[a] Esd's on mean values have been calculated with the use of the scatter formula $\sigma = [\sum(d_i - \bar{d})^2/(N-1)]^{1/2}$, where d_i is the *i*th and $\bar{d}$ is the mean of *N* equal measurements.

given in Tables II and III and important distances and angles in Tables IV and V.

Results and Discussion

The title compounds were prepared by the action of the appropriate phenylgermanium chloride on the ammonium salt of *O,O′*-dimethyl dithiophosphoric acid in benzene:

$$(C_6H_5)_3GeCl + NH_4S_2P(OCH_3)_2 \rightarrow \underset{A}{(C_6H_5)_3GeS_2P(OCH_3)_2} + NH_4Cl \quad (1)$$

$$(C_6H_5)_2GeCl_2 + 2NH_4S_2P(OCH_3) \rightarrow \underset{B}{(C_6H_5)_2Ge[S_2P(OCH_3)_2]_2} + 2NH_4Cl \quad (2)$$

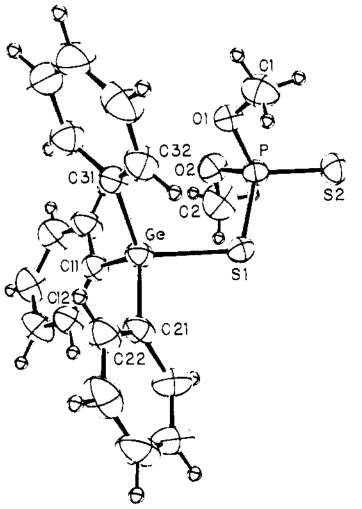

Figure 1. ORTEP drawing of $Ph_3GeS_2P(OMe)_2$ (A) showing the atomic numbering scheme. Ellipsoids represent 50% probability surfaces.

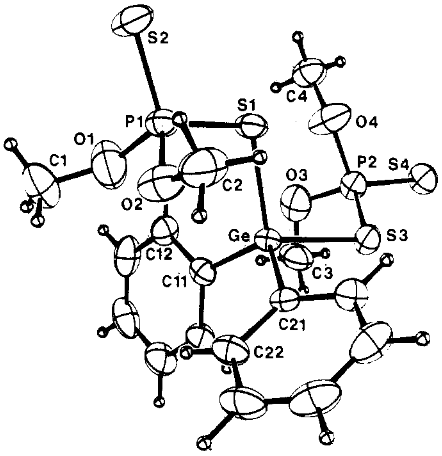

Figure 2. ORTEP drawing of $Ph_2Ge[S_2P(OMe)_2]_2$ (B) showing thermal ellipsoids of 30% probability.

The reactions were carried out under vacuum in a special vessel suitable for on-line filtration (fine frit). Both A and B are air-stable and mildly hygroscopic compounds. The compounds are highly soluble in common organic solvents, thus suggesting that they are neither polymeric nor ionic. Indeed, the spectroscopic results suggested, as shall be discussed shortly, that the dithiophosphate groups were bonded in a similar manner in both compounds in contrast to the case for the tin analogues.[12,13] Thus it seemed appropriate to determine their crystal structures, which we describe first.

Description of the Structures. Both A and B crystallize in the $P\bar{1}$ space group, and their respective asymmetric units are illustrated in Figures 1 and 2. The dithiophosphate groups are clearly monodentate, with the nonbonded sulfur atom twisted as far away as possible. The structure of A is notably similar to that of its tin analogue, $(C_6H_5)_3SnS_2P(OC_2H_5)_2$, which is described as one of a kind among organotin dithiophosphates.[12] On the other hand, the tin analogue for B, $(C_6H_5)_2Sn[S_2P(OC_3H_7\text{-}i)_2]_2$, is fully bidentate with the tin atom in an octahedral environment with the C–Sn–C angle opening up to 180°.[13] Thus it is strikingly different from B.

The geometry around the germanium atom in both compounds is that of a distorted tetrahedron. The spatial requirements of the phenyl groups appear to be greater than those of the dithiophosphate because the C–Ge–C angle in B is appreciably larger (115.8 (3)°) than the S–Ge–S angle (103.4 (1)°). In A the average value for the three C–Ge–C angles is 112.3° while that of the three C–Ge–S angles is 106.3°. Alternatively, it could be argued that this is precisely what is expected from Bent's rule.[16,17]

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Table VI. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR Chemical Shifts (ppm) for $(C_6H_5)_3GeS_2P(OCH_3)_2$ and $(C_6H_5)_2Ge[S_2P(OCH_3)_2]_2$[a]

		$(C_6H_5)_3GeS_2P(OCH_3)_2$	$(C_6H_5)_2Ge-[S_2P(OCH_3)_2]_2$
^1H NMR	OCH_3	3.27 d [6 H] ($^3J_{POCH}$ = 15.0)	3.29 d [12 H] ($^3J_{POCH}$ = 15.6)
	C_6H_5	7.2–7.6 [15 H]	7.2–7.7 [10 H]
^{13}C NMR	OCH_3	58.54 d ($^2J_{POC}$ = 5.9)	53.96 d ($^2J_{POC}$ = 7.3)
	C_6H_5	128.5, 130.3, 134.5, 135.0	128.4, 131.0, 134.7
^{31}P NMR	P[b]	94.12	91.35

[a] d = doublet; number of hydrogen atoms in brackets; coupling constants (in Hz) in parentheses. [b] The ^{31}P NMR chemical shift for $NH_4S_2P(OCH_3)_2$ in D_2O appears at 95.61 ppm downfield from 85% H_3PO_4.

The three C–Ge–S bond angles in B vary considerably from 98.7 (1)° to 111.9 (1)°. The smallest angle corresponds to the side of the "tetrahedron" away from the methoxy groups of the dithiophosphate ligand, where there is clearly least steric hindrance. The Ge–S bond lengths in these compounds are comparable to that found in $(CH_3)_2Ge(Cl)S_2CN(CH_3)_2$.[18] The average bond lengths of groups around germanium are slightly shorter in B than in A. Thus, the Ge–S bond length in A is 2.285 (1) Å while in B they are 2.257 (2) and 2.253 (2) Å. Similarly, the average Ge–C bond length in A is 1.94 Å, whereas it is 1.931 (2) Å in B. This shortening of all bonds, as the more electronegative dithiophosphate replaces a phenyl group, is to be expected from the same phenomenon noted for the methylgermanium halide series.[19] As with the C–Ge–S bond angles, the C–Ge bond lengths show more variation in A than in B. Such distortions as do occur in B are apparently centered more in the dithiophosphate groups. Within the distorted tetrahedron around phosphorus, the more electronegative groups again have the smaller bond angles in accord with Bent's rules,[16,17] the O–P–O angle being 95.7 (2)° in A and 97.1 (5) and 98.3 (4)°, respectively, in the two dithiophosphate groups in B. The crowding in B is reflected in the considerable distortion and dissimilarity of the two dithiophosphate groups. Thus, for example in A, the P–O–C angles are 120.2 (3) and 121.1 (4)° with the P–O bond lengths being 1.580 (3) and 1.578 (3) Å. In B, the dithiophosphate group containing P(1) has P–O–C angles of 127.4 (8) and 119.1 (6)° and P–O bond lengths of 1.609 (8) and 1.520 (6) Å while in that containing P(2), the P–O–C angles are 125.2 (7) and 118.4 (7)° with P–O bond lengths of 1.614 (7) and 1.530 (7) Å. The longer P–O distances are associated with the shorter O–C distances. These distortions, which appear to be centered around the P–O–C rather than S–P–S linkages, have not been reported for the similar tin and lead compounds.

The terminal P–S bonds (designated as P═S) are shorter than the bridging P–S bonds. In A the bond lengths are 1.923 (2) and 2.060 (2) Å and in B 1.898 (3) and 2.043 (3) Å for P(1) and 1.904 (3) and 2.045 (3) Å for P(2). The P═S distances are comparable to those found in nonmetal systems exemplified by $[S_2P(OC_3H_7\text{-}i)_2]_2$ (where P═S is 1.908 (3) Å)[20] and $\overline{SCH_2CH_2SP}(S)Cl$ (where P═S is 1.910 (5) Å).[21] In metal dithiophosphates, irrespective of their mode of bonding, the P–S distances only undergo relatively small changes. In general, however, the P═S bonds are usually longer than observed in A or B as exemplified by those found in $V[S_2P(OC_2H_5)_2]_3$ (average 1.971 (9) Å)[22] or $Ni[S_2P(OC_2H_5)_2]_2$ (average 1.97 (2) Å).[23] Even in the tin

Table VII. Infrared and Raman Spectra[g] of Germane Compounds

$(C_6H_5)_3GeSP({=}S)(OCH_3)_2$ (A)			$(C_6H_5)_3GeCl$		$CH_3SP({=}S)(OCH_3)_2$	$(C_6H_5)_2GeCl_2$		$(C_6H_5)_2Ge[SP({=}S)(OCH_3)_2]_2$ (B)		
IR	Raman	assignt	IR[a]	Raman	IR/Raman[b]	IR[a]	Raman	assignt	IR	Raman
1332 w	1330 (4)	o	1335 mw	1330 (3)	...	1334 m	no	o	1333 mw	1330 (4)
1302 mw	1300 (2)	w + i	1302 m	1300 (2)		1307 m	no	w + i	1301 w	1300 (4)
1169 mw	1181 (8)	a	1182 mw	1180 (8)		1181 m	1180 (6)	a		1181 (12)
1156 w	1153 (12)	c	1156 w	1153 (12)		1157 w	1157 (5)	c	1167 m, br	1151 (12)
1086 ms	1085 (12)	q	1094 vs	1082 (10)		1095 vs	1086 (11)	q	1083 m	1078 (9)
1067 mw	1067 (4)	d	1067 w	1067 (2)						
	1040 (3)	$\nu(O{-}CH_3)_{asym}$	...	...	1040 sh (13)	...	...	$\nu(O{-}CH_3)_{asym}$		1040 (7)
	1022 (24)	b and	1025 m	1022 (20)		1024 m	1028 (24)	b and	1024 s, br	
1009 s, vb		$\nu(O{-}CH_3)_{sym}$			1022 s (12)			$\nu(O{-}CH_3)_{sym}$		1022 (28)
991 s	997 (100)	p	998 s	997 (100)	...	996 s	997 (100)	p	984 sh	994 (100)
817 s	820 (4)	$\nu(PO_2)_{asym}$	...	...	831 s (12)	...	...	$\nu(PO_2)_{asym}$	806 s, br	810 (4)
788 sh	806 (4)	$\nu(PO_2)_{sym}$	...	...	815 vs (8)	...	...	$\nu(PO_2)_{sym}$	790 sh	792 (10)
739 s	no	f	735 s	no		732 vs	no	f	735 vs	no
692 s	690 (4)	v	693 vs	no	[692 m (100)][c]	693 vs	no	v	689 m	no
671 mw	664 (20)	r	678 m	665 (20)	...	671 sh	670 (24)	r	671 sh	667 (25)
644 s	641 (50)	$\nu(P{=}S)$	...	...	662 vs (80)	...	...	$\nu(P{=}S)$	645 s, br	648 (80)
614 sh	612 (12)	s	615 w	615 (11)	...	610 w	614 (6)	s	615 vw	612 (8)
496 ms	494 (18)	$\nu(P{-}S)$	...	...	502 m (20)	...	...	$\nu(P{-}S)$	522 s, br	526 (35)
461 s	450 (4)	y	460 vs	450 (2)	...	454 s	no	y	458 m	no
399 m	392 (12)	$\nu(POC)$ and	...	...	392 s (25)	[398 b, vs][d]	[394 (60)][d]	$\nu(Ge{-}S)$ and	392 m	385 (60)
370 m	367 (24)	$\nu(Ge{-}S)$	[377 vs][f]	[366 (36)][f]	372 m (20)	...	...	$\nu(POC)$	371 sh	371 (40)
331 ms	no	t + $\nu(PO_2)$	325 vs	328 (5)	339 w (7)	332 s	330 (2)	t + $\nu(PO_2)$	329 m	329 (15)
260 m	no	u?	268 m	260 (24)	...	270 m	271 (44)	u?	271 w	274 (25)

[a] See ref 28. [b] See ref 29. [c] S—CH_3, hence not expected in A or B. [d] Ge–Cl, hence not expected in A or B. [e] S–Ge–S in $(CH_3)_3Ge{-}SCH_3$ is at 394 cm^{-1}.[30] [f] Ge–Cl, hence not expected in A or B. [g] Frequencies in cm^{-1} and Raman intensities in parentheses; no = not observed.

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Table VIII. Mass Spectra of $(C_6H_5)_3GeSP(S)(OCH_3)_2$ (A) and $(C_6H_5)_2Ge[SP(S)(OCH_3)_2]_2$ (B)

ion family[a] (A)	*m/z*	Int(A)	% RA(A)	Int(B)	% RA(B)	ion family (B)
	464	47				
	463	34				
$(C_6H_5)_3GeSP(S)(OCH_3)_3)_2^+$	462	175	9.8			
	461	46				
	460	129				
	459	15				
	458	75				
	387	111		306		
	386	80		219		
$(C_6H_5)_2GeSP(S)(OCH_3)_2^{+\cdot}$	385	482	26.4	1000	70.7	$(C_6H_5)_2GeSP(S)(OCH_3)_2^{+\cdot}$
	384	118		346		
	383	362		805		
	382	41		90		
	381	190		570		
	355	24				
	354	21				
$(C_6H_5)_2GeSP(OCH_3)_2^+$	353	103	7.1			
	352	37				
	351	74				
	350	18				
	349	56				
	307	160				
	306	131				
$(C_6H_5)_3Ge^{+}$[b]	305	533	36.8			
	304	219				
	303	519				
	302	64				
	301	292				
	231			72		
	230			28		
	229	47		185	13.6	$(C_6H_5)_2GeH^+$
	228	34		58		
$C_6H_5GeC_6H_4^+$	227	84	6.9	172		
	226	60		23		
	225	79		105		
	224	26				
	223	30				
$C_{12}H_{10}^{+\cdot}$	154	129	2.5			
	153	48		24		
	152	34		18		
$C_6H_5Ge^+$	151	102	6.7	78	5.0	$C_6H_5Ge^+$
	150	29		20		
	149	79		57		
	148	10		10		
	147	57		40		
$SP(OCH_3)_2^+$	125	123	2.3	256	5.4	$SP(OCH_3)_2^+$
$P(OCH_3)_2^+$	93	82	1.5	250	5.3	$P(OCH_3)_2^+$

[a] Germanium isotopes exist in the following percentage abundances: 70, 20.55%; 72, 27.37%; 73, 7.61%; 74, 36.74%; 76, 7.67%. Hence the ion family is placed opposite the species containing germanium-74. [b] This gives the poorest fit of the theoretical distribution of all the peaks but is still acceptable at 3.3%.

analogue of A, $(C_6H_5)_3SnS_2P(OC_2H_5)_2$, the P═S distance is 1.931 (1) Å.[12] Apparently, the shortest P═S bond reported previously is in $Te[S_2P(OCH_3)_2]_2$ (1.923 (7) Å), which also has monodentate ligands.[1]

The contrast between the structure of B and that of the similar tin compound is particularly surprising in view of the similarity between the structure of A and that of triphenyl (*O,O'*-diethyl dithiophosphato)tin.[12] The structure of $(C_6H_5)_2Sn[S_2P(OC_3H_7\text{-}i)_2]_2$[13] consists of octahedrally coordinated tin with the phenyl groups trans to one another and with symmetrically chelating dithiophosphate ligands. The tin atoms are related by a unit translation along the *c* axis (6.341 (8) Å), thereby making the structure a virtual polymer. This is in total contrast to the structure of B, in which, as in A, the P═S bonds are located well away from the germanium atom and indeed are well away from adjacent molecules. The shortest Ge- - -S intermolecular distance in A is 5.253 (1) Å and in B is 5.363 (2) Å, both of which are considerably greater than the sum of the van der Waals radii of 3.85 Å. This isolation of the P═S bond may account for the fact that it is relatively short. There is clearly no indication of even the anisobidentate behavior found for the sulfur ligand in $(CH_3)_2Ge(Cl)S_2CN(CH_3)_2$.[18]

The spectroscopic data will now be discussed in light of the structural determinations even though chronologically it was the spectroscopic evidence that suggested to us the possibility that the structures could be very similar.

NMR Spectra. The ^1H NMR spectra of both compounds (Table VI) show the CH_3 peaks as doublets centered at 3.3 ppm downfield of Me_4Si with long-range ^3J(P–O–C–H) coupling[24] of 15 Hz, very similar to the values in $(C_6H_5)_3SnS_2P(OCH_3)_2$. However, it is possible that these parameters show only small variations with mode of coordination.[13,25] The $^{13}C\{^1H\}$ NMR spectra (Table VI) are also similar for both A and B, with the CH_3 peaks appearing as doublets ($|^2J$(P–O–C)$|$ = 5.9 and 7.3 Hz

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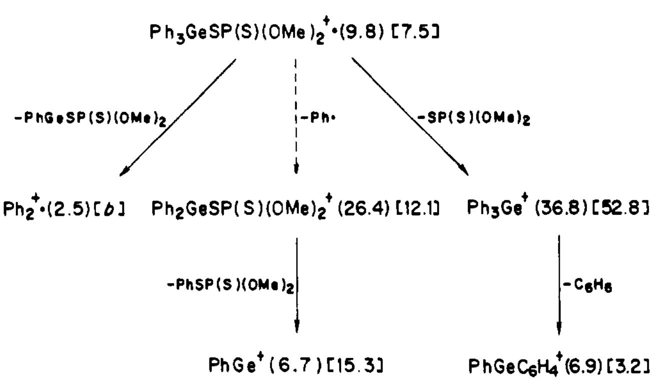
Scheme I[a]



[a] Values of % RA for $Ph_3GeSP(S)(OMe)_2$ are given in parentheses and for the corresponding Ph_3GeBr species in brackets.[31] [b] The formation of $Ph_2{}^{+\cdot}$ was metastable confirmed for the bromide, but the % RA value was not given.

for A and B, respectively) and the phenyl carbon peaks in the expected 130–140 ppm region.[26] The $^{31}P\{^1H\}$ NMR spectra (Table VI) are seen as sharp singlets in both A and B at 94.12 and 91.35 ppm, respectively, downfield from external H_3PO_4, both values being typical of thio acids of phosphorus containing a P=S bond. The similarities suggested the similar environments of these monodentate ligands.

Vibrational Spectra. The main features of the IR and Raman spectra of A and B are displayed in Table VII for the region 1300–250 cm^{-1}. The spectra of both compounds are very similar, being dominated by bands characteristic of a monosubstituted benzene ring which are known to be relatively insensitive to the nature of the substituent.[27] An extensive study of $(C_6H_5)_3MX$ and $(C_6H_5)_2MX_2$ species, which centered on germanium derivatives,[28] emphasized the consistent nature of the phenyl vibrations and illustrated that assignments should be made to the $(C_6H_5)_3Ge$ and $(C_6H_5)_2Ge$ moieties as a whole. No specific assignments to $\nu(GeC_3)$ can be expected. The assignments made in Table VII to these moieties use the same alphabetic notation as in ref 28. The inclusion of the previous assignments of $(C_6H_5)_3GeCl$ and $(C_6H_5)_2GeCl_2$ along with the unreported Raman data and the assignments for $CH_3SP(=S)(OCH_3)_2$[29] makes the assignments of A and B essentially self-evident, with the exception of those discussed below. Earlier work on many $R_3SnSP(=S)(OR_2')_2$ species[9] has raised the question of whether $\nu(O-CH_3)$ bands should be assigned to the 1170–1095-cm^{-1} or to the 1015–965-cm^{-1} region. Related to this is the question of whether the $\nu(PO_2)$ modes are more appropriately placed in the 1015–965-cm^{-1} or in the 875–730-cm^{-1} region. A glance at Table VII indicates that $\nu(PO_2)$ must correspond to the peaks close to 800 cm^{-1} in both A and B because no phenyl peaks occur in this region and $\nu(PO_2)$ can also be seen clearly in the ammonium salt of dithiophosphate and the free acid. The region 1180–980 cm^{-1} is crowded with distinctive phenyl bands, notably the very intense Raman band at ca. 997 cm^{-1} (p) and the intense infrared feature at ca. 1095 cm^{-1} (q). However, only in the spectra of A and B is there a strong *broad* feature in the 1009- and 1024-cm^{-1} region that is also seen in the ammonium salt and free acid. Thus this region is chosen for the $\nu(O-CH_3)$ assignment where there is overlapping with b and possibly p. As with the $\nu(PO_2)$ modes, the assignment of $\nu(P=S)$ to 644 cm^{-1} (641 cm^{-1} Raman) in A and 645 cm^{-1} (648 cm^{-1} Raman) in B is clear and unequivocal.[9,29] In the ammonium salt, which presumably does not contain an isolated P=S bond, this peak is not evident whereas it is a strong feature in the free acid, which does. The next clear feature at 496 cm^{-1} (494 cm^{-1} Raman (A) and 522 cm^{-1} (526 cm^{-1} Raman) (B) corresponds to the $\nu(P-S)$ vibration. The similarity of these modes to those seen in $CH_3SP(=S)(OCH_3)_2$ initially suggested to us that there might be simple monodentate linkages present in both A and B. The *average* values for these two modes, which must be related, are 569 cm^{-1} in A and 585 cm^{-1} in B. The higher frequency in B is consistent with the shorter and hence presumably stronger P–S bonds in B relative to those in A. The bands at ca. 370 and 390 cm^{-1} in both A and B clearly correspond to the deformation modes of $\delta(POC)$.[29] However, the $\nu(Ge-S)$ vibration is also expected in this region because in species such as $R_3Ge-SCH_3$ it is clearly identifiable as a sharp, relatively intense band at ca. 390 cm^{-1} in the Raman effect.[30] The two Ge–S bonds in B should lead to two separate bands, so we can really not go beyond assigning the $\delta(POC)$ and $\nu(GeS)$ modes as overlapping in this region, although the relative intensity of the Raman bands makes 367 cm^{-1} the more likely assignment for $\nu(GeS)$ in A and 385 cm^{-1} in B. This would be consistent with the shorter Ge–S bonds in B.

Mass Spectra. As may be observed from Table VIII, the electron impact mass spectra of the two compounds are relatively simple. The spectrum of A may be compared to those of other $(C_6H_5)_3GeX$ species (X = H, Cl, Br, I) where fragmentation pathways were determined with use of metastables.[31] On the basis of the major routes proven for $(C_6H_5)_3GeBr$, we can essentially superimpose a pattern for A in Scheme I.

The fragmentation pattern of B is even simpler than that of A. No parent peak is observed, as was also noted for $(C_6H_5)_3GeI$.[31] By far the most prominent peak is $(C_6H_5)_2GeSP(S)(OCH_3)_2{}^+$, indicating the clear preference for the loss of the dithiophosphate group rather than the phenyl ring. The peaks associated with dithiophosphate fragmentation are again seen as for A. Thus the mass spectra initially suggest what we subsequently confirmed, namely that we are dealing with molecules that have similar linkages with monodentate ligands.

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Registry No. A, 97390-98-2; B, 97390-99-3.

Supplementary Material Available: Unit cell packing diagrams and tables of anisotropic thermal parameters, hydrogen atom coordinates and isotropic thermal parameters, and observed and calculated structure factors (40 pages). Ordering information is given on any current masthead page.

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