Journal of Organometallic Chemistry, 323 (1987) 271–283
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

PREPARATION AND CHARACTERIZATION OF ORGANOGERMANIUM *O,O'*-DIMETHYL AND DIETHYL-DITHIOPHOSPHATES

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(Received July 17th, 1986)

Summary

Organogermanium derivatives of dithiophosphoric acid of general formula $R_{4-n}Ge[SP(S)(OR')_2]_n$, where $n = 1$–3, R = Me, Ph and R' = Me, Et, have been prepared and characterized by means of ^1H, ^{13}C NMR and vibrational spectroscopy and mass spectrometry. The spectroscopic results indicate that the dithiophosphate groups are monodentate and that an approximate tetrahedral geometry about the germanium atom is maintained. This is in part confirmed by a preliminary X-ray crystallographic determination of $PhGe[SP(S)(OMe)_2]_3$, whose crystals are orthorhombic, space group $Pn2_1a$, a 13.673(4), b 14.566(3), c 13.154(3) Å, V 2620(1) Å^3 and $Z = 4$ from 1225 observed reflections $[I > 3\sigma(I)]$.

Introduction

Various metal dithiophosphates have been reported in the literature [1,2]. The dithiophosphate ligand exhibits differing bonding modes such as monodentate [3,4], bidentate [5,6] or bridging [7]. Occasionally, both mono and bidentate [8,9] or bridging and bidentate ligands [10,11] have been found in the same compound. Because of this richness in the chemistry of metal dithiophosphates and our interest in organogermanium compounds, we recently initiated a study of organogermanium dithiophosphates and found that in $Ph_3Ge[SP(S)(OMe)_2]$ and $Ph_2Ge[SP(S)(OMe)_2]_2$ the dithiophosphate ligand adopts the normally less favored monodentate linkage [12]. In this paper, we report the synthesis and characterization of ten more compounds. Because most of them are liquids, characterization has depended on spectroscopic data which indicates that the dithiophosphate group is monodentate in all cases. We were particularly interested in obtaining a definitive structure of $PhGe[SP(S)(OMe)_2]_3$ because there is no structural data available on the tris compounds. However, despite many attempts we were only able to get a partial resolution of the structure of phenyl tris(*O,O'*-dimethyldithiophosphato)germanium (**10**).

TABLE 1

DETAILS OF REACTIONS BETWEEN ORGANOGERMANIUM CHLORIDES AND AMMONIUM *O,O′*-DIMETHYL AND DIETHYLDITHIOPHOSPHATES AND ANALYTICAL DATA OF THE PRODUCTS [a]

Product	No.	No. of mmoles		Stirring		Yield	Refrac. index *n*	Found (calc) (%)		
		germane	dithiophosphate	Temp. (°C)	Time (h)	(%)		C	H	P
$Me_3Ge[SP(S)(OMe)_2]$ [b,c]	**1**	2.0	2.4	−10	10	57	1.5343	22.20 (21.85)	5.97 (5.50)	11.68 (11.27)
$Me_2Ge[SP(S)(OMe)_2]_2$ [d]	**2**	1.0	2.9	10	12	76	1.5842	17.98 (17.28)	4.79 (4.35)	15.54 (14.86)
$MeGe[SP(S)(OMe)_2]_3$	**3**	1.0	3.2	10 [e]	6	80	1.5979	15.16 (15.04)	4.00 (3.79)	16.42 (16.62)
$Me_3Ge[SP(S)(OEt)_2]$ [b]	**4**	2.0	2.3	10	5	80	1.5196	27.62 (27.76)	5.94 (6.32)	10.47 (10.23)
$Me_2Ge[SP(S)(OEt)_2]_2$	**5**	1.3	2.8	10 [f]	4	82	1.5439	24.10 (25.39)	4.99 (5.54)	12.71 (13.09)
$MeGe[SP(S)(OEt)_2]_3$	**6**	1.0	3.7	15 [e]	5	52	1.5753	23.93 (24.27)	4.98 (5.17)	
$Ph_3Ge[SP(S)(OEt)_2]$ [g]	**7**	1.0	1.2	20	4	85		53.94 (54.02)	5.04 (5.15)	6.06 (6.33)
$Ph_2Ge[SP(S)(OEt)_2]_2$	**8**	1.1	2.4	20 [e]	10	80	1.6080	39.84 (40.22)	4.81 (5.06)	9.78 (10.37)
$PhGe[SP(S)(OEt)_2]_3$	**9**	1.1	3.1	15 [e]	10	72	1.5960	30.31 (30.65)	4.49 (5.00)	
$PhGe[SP(S)(OMe)_2]_3$ [h]	**10**	1.0	3.3	20	6	63		23.20 (23.20)	3.71 (3.73)	

[a] All compounds except **7** and **10** were liquids at R.T. [b] Starting material was trimethyl germanium bromide. [c] Boils at 84 °C/0.2 mmHg. [d] M.p. 0 °C. [e] The contents of reaction flask were frozen at −196 °C during addition. [f] Occasionally cooled to −10 °C. [g] M.p. 115 °C recrystallized from CS_2. [h] M.p. 55 °C.

Experimental

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 phenyl and methylgermanium chlorides (Alfa) and the ammonium salt of *O,O'*-dimethyl and diethyldithiophosphoric acid (Aldrich) suggested that 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 refractive indices were taken on a Bausch and Lomb refractometer and were corrected to 25 ° C. 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 capillary tubes 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 at ambient temperature and a frequency of 60 MHz on a Varian EM-360 spectrometer in CS_2 using tetramethylsilane as an internal standard. $^{13}C\{^1H\}$ NMR spectra were recorded, at ambient temperature and a frequency of 22.64 MHz on a Bruker CXP-100 FT spectrometer in $CDCl_3$ solutions. For ^{13}C NMR spectra, the central line of the $CDCl_3$ signal at 77.12 ppm was used as internal standard. The mass spectra were recorded at 70 eV on a Varian GMAT-CH5 double-focusing mass spectrometer.

Preparation of organogermanium dialkyldithiophosphates (1–10)

Typically, a solution of 1–2 mmol of the appropriate organogermanium chloride and benzene (2–3 ml) were added to 1–4 mmol of the dry salt $(CH_3O)_2PS(S)NH_4$ or $(C_2H_5O)_2PS(S)NH_4$ under dry nitrogen. The reaction vessel was warmed up to between -10 and 20 ° C and the mixture was stirred for 4–10 h. The solid ammonium chloride was filtered off and the filtrate was slowly evaporated under vacuum to obtain the desired organogermanium dithiophosphates. The details of these reactions are given in Table 1.

For $PhGe[SP(S)(OMe)_2]_3$ (**10**) attempts were made to prepare crystals of appropriate quality to allow us to carry out X-ray crystallographic analysis. The best of these attempts used a solution of $C_6H_5GeCl_3$ (0.248 g, 0.97 mmol) in C_6H_6 (2.5 ml) added under nitrogen to the previously dried salt, $(CH_3O)_2PS(S)NH_4$ (0.571 g, 3.30 mmol). The contents were immediately frozen (-196 ° C) and the reaction vessel evacuated. The reaction mixture was warmed up to ambient temperature and stirred with occasional cooling for 6 h prior to filtration. The solvent was immediately evaporated off under vacuum. The quasi-solid white residue of compound, **10**, was recrystallized from CS_2 in the refrigerator. Yield 63%, m.p. 55 ° C. Anal. Found: C, 23.20; H, 3.71. $C_{12}H_{23}S_6P_3O_6Ge$ calc: C, 23.20; H, 3.73%.

*Attempted X-ray crystallographic analysis of **10***

Crystals consistently deteriorated during data collection. Higher angle intensities, beyond $2\theta = 35°$, rapidly decreased in intensity and many had to be rejected on the basis of peak profile analysis. The following describes the best results we were able to achieve which gave us a partial solution of the structure.

TABLE 2

SUMMARY OF CRYSTAL DATA, INTENSITY COLLECTION, AND STRUCTURAL REFINEMENT FOR $C_6H_5Ge[SP(S)(OCH_3)_2]_3$

Cell constants	13.673(4), 14.566(3), 13.154(3) Å
Cell volume (Å^3)	2620(1)
Crystal system	orthorhombic
Space group	$Pn2_1a$
Mol. wt.	621.2
Z, F (000)	4, 1264
ρ_c, ρ_o (g cm^{-3})	1.57, 1.55
Cryst. dimens. (mm)	0.25×0.28×0.43
Abs. coeff. μ(cm^{-1})	17.59
Min. abs. corr.	1.515
Max. abs. corr.	1.783
Radiation	Mo-K_α, $\lambda = 0.71069$ Å
Monochromator	highly oriented graphite
Temp (°C) [a]	24
2θ angle (°)	4–50
Scan type	coupled θ (crystal)/2θ (counter)
Scan width	$K_{\alpha_1} - 1$ to $K_{\alpha_2} + 1°$
Scan speed (° min^{-1})	variable, 2.02–4.88
Bkgd time/scan time	0.5
Total reflcns. measd	2765 ($+h$, $+k$, $+l$)
Unique data used	1225 [$I > 3\sigma(I)$]
No. of parameters (NP)	135
$R = (\Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|)$ [b]	0.0940
$R_w = [\Sigma\omega(\|F_o\| - \|F_c\|)^2/\Sigma\omega\|F_o\|^2]^{1/2}$ [b]	0.0981
$\Delta\rho_{max}$ (eÅ^{-3})	1.3
Shift: error (max)	0.2

[a] We have no facilities to carry out low temperature structure determinations. [b] The best results we were able to achieve with Ge and S atoms anisotropic and the ratio of unique data to NP is approximately 9:1.

The crystal was sealed in a capillary tube and mounted on a Syntex P2$_1$ diffractometer for X-ray data collection; details of the method of data collection have been given previously [13]. The least squares refinement on the setting angles of 25 high angle reflections ($15 < 2\theta < 30°$) yielded the cell constants given in Table 2. The intensities of three monitor reflections decreased by approximately 3.5% and an appropriate scaling factor was applied to correct this. The data was further corrected for Lorentz and polarization effects and analytical absorption corrections were applied. The details of other pertinent X-ray data are given in Table 2.

Analysis of the systematic absences ($0kl$, $k + l = 2n + 1$; $hk0$, $h = 2n + 1$) indicated that the space group was either $Pnma$ (D_{2h}^{15}, No. 62) or $Pn2_1a$ (standard setting $Pna2_1$ (C_{2v}^{9}, No. 33)). Attempts were made to solve the structure by using the conventional heavy atom techniques in both plausible space groups. Subsequent Fourier maps revealed the positions of the remaining atoms but unfortunately a satisfactory refinement could not be achieved, although the best solution was achieved in $Pn2_1a$.

The refinement minimizing $(|F_o| - |F_c|)^2$ never converged to values of R and R_w less than 0.08 even when P and O were also refined anisotropically. However, extending anisotropic refinement beyond Ge and S reduced the ratio of unique data to the number of parameters to an unacceptable level. However, it was at least clear that the dithiophosphate groups are monodentate, with the environment about germanium being that of a slightly distorted tetrahedron and with an average Ge–S bond length of 2.25 Å *.

Results and discussion

The organogermanium dithiophosphate esters were prepared by nucleophilic replacement of one or more halogens on organogermanium compounds by *O,O'*-dimethyl or diethyl dithiophosphate anions, as summarized below:

$$PhGeCl_3 + 3(MeO)_2PS(S)NH_4 \rightarrow PhGe[SP(S)(OMe)_2]_3 + 3NH_4Cl \qquad (1)$$

$$R_{4-n}GeX_n + n(R'O)_2PS(S)NH_4 \rightarrow R_{4-n}Ge[SP(S)(OR')_2]_n + nNH_4Cl \qquad (2)$$

$(R = Me, Ph;\ R' = Me, Et;\ n = 1, 2, 3)$

The compounds **1–10** (see Table 1) are air stable, moderately hygroscopic, highly soluble in common organic solvents and have a repulsive odor. Only one of the compounds, trimethyl (*O,O'*-dimethyldithiophosphato)germanium (**1**) could be distilled without decomposition, and for all of the others decomposition preceded distillation. Thus, for example when an attempt was made to distil dimethylbis(*O,O'*-dimethyldithiophosphato)germanium (**5**), the pressure fluctuated drastically as soon as two drops of the compound (44° C, 0.18 mmHg) were collected, indicating decomposition was occurring. The crystals obtained from both *O,O'*-dimethyl- and *O,O'*-diethyldithiophosphoric acid salts were soft and needed special care in handling. In these reactions (1 and 2) no evidence of the formation of intermediates could be detected by ^1H NMR spectroscopy.

NMR spectra

^1H, and ^{13}C NMR spectra of the compounds are summarized in Tables 3 and 4 respectively, along with those of $(C_6H_5)_3Ge[SP(S)(OCH_3)_2]$ and $(C_6H_5)_2Ge[SP(S)(OCH_3)_2]_2$ for comparison [12]. The ^1H NMR spectrum of the *O,O'*-dimethyldithiophosphate derivatives show OCH_3 peaks as doublets due to $^3J(POCH)$ coupling while for *O,O'*-diethyldithiophosphate derivatives, the OCH_2 signals appear as multiplets due to the overlap of two quartets. The $Ge\text{-}CH_3$ and $Ge\text{-}C_6H_5$ signals are similar in both dimethyl and diethyldithiophosphates (Table 3). The chemical shift of trimethyl (0.67, 0.65 ppm), dimethyl (1.29, 1.21 ppm) and methylgermanium (1.76, 1.73 ppm) dimethyl and diethyl dithiophosphates can be compared to the chloromethylgermane series $(CH_3)_3GeCl$ (0.78 ppm), $(CH_3)_2GeCl_2$ (1.14 ppm) and CH_3GeCl_3 (1.58 ppm) [14]. Thus, the effect of the dithiophosphate group can be best described as that of a halogen atom with an electronegativity close to that of chlorine.

Similar conclusions can be drawn from the $^{13}C\{^1H\}$ NMR data. The $Ge\text{-}CH_3$ chemical shifts of trimethyl (3.2, 3.6 ppm), dimethyl (9.2, 9.3 ppm) and methyl (13.7, 15.9 ppm) germanium dithiophosphates are similar to those of the corresponding chloromethylgermanes, $(CH_3)_3GeCl$ (4.8 ppm), $(CH_3)_2GeCl_2$ (10.7 ppm) and CH_3GeCl_3 (15.9 ppm) [14]. All other ^{13}C signals (Table 5) appear as and where expected.

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* The ORTEP diagram can be obtained from one of the authors (J.E.D.).

TABLE 3

^{1}H NMR DATA [a,b]

Compound	No.	δ(Ge–CH_3/C_6H_5)	δ(O—CH_3)	^3J(POCH)
$(CH_3)_3Ge[SP(S)(OCH_3)_2]$	**1**	0.67(9H)	3.59(6H,d)	14.4
$(CH_3)_2Ge[SP(S)(OCH_3)_2]_2$	**2**	1.29(6H)	3.69(12H,d)	15.0
$CH_3Ge[SP(S)(OCH_3)_2]_3$	**3**	1.76(3H)	3.73(18H,d)	15.6
$(CH_3)_3Ge[SP(S)(OC_2H_5)_2]$	**4**	0.65(9H)	3.96(4H,m)	1.25(6H,t)
$(CH_3)_2Ge[SP(S)(OC_2H_5)_2]_2$	**5**	1.21(6H)	4.07(8H,m)	1.25(12H,t)
$CH_3Ge[SP(S)(OC_2H_5)_2]_3$	**6**	1.73(3H)	4.03(12H,m)	1.33(18H,t)
$(C_6H_5)_3Ge[SP(S)(OC_2H_5)_2]$	**7**	7.1–7.6(15H)	3.70(4H,m)	0.89(6H,t)
$(C_6H_5)_2Ge[SP(S)(OC_2H_5)_2]_2$	**8**	7.1–7.7(10H)	3.67(8H,m)	0.97(12H,t)
$C_6H_5Ge[SP(S)(OC_2H_5)_2]_3$	**9**	7.2–7.9(5H)	4.03(12H,m)	1.17(18H,t)
$(C_6H_5)_3Ge[SP(S)(OCH_3)_2]$ [d]	–	7.2–7.6(15H)	3.27(6H,d)	15.0
$(C_6H_5)_2Ge[SP(S)(OCH_3)_2]_2$ [d]	–	7.2–7.7(10H)	3.29(12H,d)	15.6
$C_6H_5Ge[SP(S)(OCH_3)_2]_3$	**10**	7.3–7.8(5H)	3.33(18H,d)	16.0

[a] For $NH_4S_2P(OC_2H_5)_2$ in D_2O, the OCH_2 and CH_3 peaks appear at 3.98(m) and 1.22 (t, *J* 7 Hz) in reference to $(CH_3)_3Si(CH_2)_2CO_2Na$. [b] All spectra were run in CS_2. Chemical shifts in ppm and coupling constants in Hz. [c] Multiplets arising from doublet of quartets. [d] See reference [12].

The similarity of the spectra of compounds **1**–**10** to those of the two compounds for which we already have crystal structures that confirm monodentate linkages [12] along with the similarity in trends with the $(CH_3)_xGeCl_{4-x}$ series suggests that all

TABLE 4

^{13}C NMR DATA [a,b]

Compound	No.	δ(Ge-CH_3/C_6H_5)	δ(OCH_3/OCH_2)	^2J(POC)	δ(CH_3)
$(CH_3)_3Ge[SP(S))OCH_3)_2]$	**1**	3.2	53.3		
$(CH_3)_2Ge[SP(S)(OCH_3)_2]_2$	**2**	9.2	54.1		
$CH_3Ge[SP(S)(OCH_3)_2]_3$	**3**	13.7	54.4		
$(CH_3)_3Ge[SP(S)(OC_2H_5)_2]$	**4**	3.6	63.6(d)	7.4	15.9
$(CH_3)_2Ge[SP(S)(OC_2H_5)_2]_2$	**5**	9.3	64.2(d)	7.4	15.9
$CH_3Ge[SP(S)(OC_2H_5)_2]_3$	**6**	15.9	64.6(d)	5.9	15.9
$(C_6H_5)_3Ge[SP(S)(OC_2H_5)_2]$	**7**	128.5, 130.2 134.7, 135.1	63.7(d)	5.9	15.7
$(C_6H_5)_2Ge[SP(S)(OC_2H_5)_2]_2$	**8**	128.4, 128.8 130.9, 131.4 133.6, 134.4 134.8	64.0(d)	5.9	15.5
$C_6H_5Ge[SP(S)(OC_2H_5)_2]_3$	**9**	128.1, 128.6 131.3, 131.9 132.9, 134.0 136.7	64.6(d)	4.4	15.8
$(C_6H_5)_3Ge[SP(S)(OCH_3)_2]$ [d]	–	128.5, 130.3 134.5, 135.0	58.5(d)	5.9	
$(C_6H_5)_2Ge[SP(S)(OCH_3)_2]$ [d]	–	128.4, 131.0 134.7	54.0(d)	7.3	
$C_6H_5Ge[SP(S)(OCH_3)_2]_3$ [c]	**10**	128.4, 128.8 131.6, 132.0 132.9, 133.8	54.5(d)	7.4	

[a] The O-CH_3 peak of $NH_4S_2P(OCH_3)_2$ in D_2O appears at 53.7(d, *J* 7.4 Hz) in reference to dioxane (67.4 ppm). [b] All spectra were recorded in $CDCl_3$. [c] For $C_6H_5GeCl_3$ the signals are 129.7, 131.5, 133.2 and 135.2. [d] See reference [12].

of them have monodentate linkages with the environment about germanium being that of a slightly distorted tetrahedron.

Infrared and Raman spectra

The essential features of the IR and Raman spectra are recorded in Tables 5 and 6 for the methyl- and phenyl-germanium derivatives, respectively. Once again the data for $(C_6H_5)_3Ge[SP(S)(OCH_3)_2]$ and $(C_6H_5)_2Ge[SP(S)(OCH_3)_2]_2$ is included for comparison [12]. For the methylgermane derivatives, the spectra may be considered as superimpositions of the methylgermane features onto those of the dithiophosphate moiety. For the dithiophosphates containing Ge–C_6H_5 groups, the spectra are dominated by bands of mono-substituted benzene rings, which are relatively insensitive to the dithiophosphate group [15]. An extensive study of the vibrational spectra of $(C_6H_5)_3GeX$, $(C_6H_5)_2GeX_2$ and $C_6H_5GeX_3$ emphasized this fact and illustrated that assignments should be made to the phenylgermane group as a whole, and no distinction on the basis of the number of phenyl groups can be made [16–18]. Therefore, no specific assignments to the $\nu(Ge{-}C_2)$ or $\nu(Ge{-}C_3)$ bands are made in contrast to the assignment of ν(Ge–C) bands in the methylgermanes. Thus, after assigning the bands for methyl- and phenyl- germanes it becomes quite straightforward to assign bands due to the dithiophosphate group. The compounds show $\nu(O{-}CH_3)$ around 1000 cm^{-1}, $\nu(PO_2)$ in the 800 cm^{-1} region, a clear distinctive terminal ν(P = S) band around 650 cm^{-1} and the bridging ν(P–S) stretches appear in the 525–490 cm^{-1} region. These bands are to be expected for monodentate dithiophosphates [19] because in the ammonium salt of *O,O'*-dimethyldithiophosphoric acid, which presumably does not contain an isolated P=S bond, these bands are not evident and in the free acid and the ester, $(CH_3O)_2P(S)SCH_3$, [20] the ν(P=S) and the ν(P–S) bands are clear features.

The similarity of the ν(Ge–C) symmetric and asymmetric vibrations of chloromethylgermanes [21–24] to those of the methylgermanium dithiophosphates are consistent with the assumption that the effect of dithiophosphate substitution is, in effect, equivalent to that of a chlorine atom. For example, in the spectrum of dimethyl bis(*O,O'*-dimethyldithiophosphato)germanium, **5**, the ν(Ge–C) asymmetric and symmetric stretches appear at 638 and 579 cm^{-1} and for $(CH_3)_2GeCl_2$ the corresponding bands are observed at 640 and 594 cm^{-1} respectively. In trimethyl(*O,O'*-dimethyldithiophosphato)germanium (**1**), these values are 609 and 568 cm^{-1} compared to 612 and 569 cm^{-1} for $(CH_3)_3GeCl$. Finally, for methyltris(*O,O'*-dimethyldithiophosphato)germanium (**3**) and methyltris(*O,O'*-diethyldithiophosphato)germanium (**6**) the values of ν(Ge–C) are 609 and 606 cm^{-1} respectively compared to 630 cm^{-1} for CH_3GeCl_3. In our earlier study on the related diphenylbis(*O,O'*-dimethyldithiophosphato)germanium [12] we concluded that ν(Ge–S), both asymmetric and symmetric where appropriate, and ρ(POC) modes are all expected in the 370–399 cm^{-1} region. In several of the compounds discussed in this paper the band in this region of the IR spectrum is very broad and ill-defined. To further complicate matters, the Raman spectrum is occasionally masked as far out as 400 cm^{-1} from the exciting line. Thus only general assignments can be made but it is reasonable to suppose that the more intense peaks in the IR spectra are centered around the asymmetric Ge–S stretch and those in the Raman effect are mainly attributable to the symmetric Ge–S stretching mode. The similarity in the

(*Continued on p. 282*)

TABLE 5

SELECTED FEATURES AND THEIR ASSIGNMENTS IN THE VIBRATIONAL SPECTRA[a] (cm^{-1}) OF COMPOUNDS 1–6

1		2		3		4		5		6		Assignments
IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	
1038sh		1036sh		1038sh		1035sh	1053(13)	1035sh	1054(30)	1039sh	1055(19)	$\nu(O{-}C)_{asym}$
1008s		1008s,br		1001sh		1008s		1008s		1001s		$\nu(O{-}C)_{sym}$
835s,		812s,sh	817(17)	820sh	812(10)	831s		821sh		820sh		$\nu(PO_2)_{asym} + \rho(CH_3Ge)$
798s,br		792br		800s,br		777s,br		786s,br		792s,br		$\nu(PO_2)_{sym} + \rho(CH_3Ge)$
655s	659(44)	650s	657(100)	648s	655(78)	657s	651(88)	644s,br	654(56)	644s	654(93)	$\nu(P{=}S)$
609s	610(29)	625sh				608s	608(23)	624sh				$\nu(Ge{-}C)_{asym}$
568s	567(100)	579w	579(66)	610sh	609(15)	566m	565(81)	584m	580(49)		606(12)	$\nu(Ge{-}C)_{sym}$
527s	522(36)	521s	521(77)	517s	519(27)	536s	524(38)	532s	525(54)	527s	526(53)	$\nu(P{-}S)$
398s	398(15)	401s	404(75)	406s		391m	[b]	309sh	[b]	398s,br		$\nu(Ge{-}S)_{asym} + \delta(POC)$
366m	362(13)	368m	366(77)	386sh	388(100)	360sh	[b]	381s,br	[b]	388sh	381(60)	$\nu(Ge{-}S)_{sym} + \delta(POC)$

[a] s, m, w = strong, medium, weak; sh = shoulder; br = broad; parentheses show relative intensities of Raman peaks. [b] Fluorescence too large to allow for assignment.

TABLE 6

SELECTED FEATURES AND THEIR ASSIGNMENTS IN THE VIBRATIONAL SPECTRA [a] (cm^{-1}) OF COMPOUND 7–**10**

7		8		9		10		A [b]		B [b]		Assignments
IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	
1020sh	1020(23)	1033sh	1021(25)	1023sh	1019(10)		1019(13)			1040(7)		1040(3)ν(O–C)$_{asym}$
									1022(28)	1009s,br	1022(24)	ν(O–C)$_{sym}$ +
1005m		1006s,br		1003s,br		1000s,br		1024br				C_6H_5 mode
992sh	995(100)	954s,br	996(100	962s,br	995(60)		992(32)	984sh	994(100)	992s	997(100)	ρ(C_6H_5 mode)
819w		819sh		819sh				806s,br	810(4)	817s	820(4)	$\nu(PO_2)_{asym}$
776m		788s,br		791s,br		781s	812(13)	790sh	792(10)	788sh	806(4)	$\nu(PO_2)_{sym}$
639m,br	647(39)	641s	651(84)	640s	652(100)		652(100)	645s,br	648(80)	644s	641(50)	ν(P=S)
508m	524(47)	529m		527m		509s	524(22)	522s,br	526(35)	496ms	494(18)	ν(P–S)
376w		395s,br	[c]	398s,br		408m		392m	385(60)	399m	392(12)	ν(Ge–S)$_{asym}$ + δ(POC)
358w	[c]	385sh	[c]	388sh	384(41)	375m	370(50	372sh	371(40)	370m	367(24)	ν(Ge–S)$_{sym}$ + δ(POC)

[a] s, m, w = strong, medium, weak; sh = shoulder; br = broad; parentheses show relative intensities of Raman peaks. [b] **A** = $(C_6H_5)_2Ge\{SP(S)(OCH_3)_2\}_2$ and **B** = $(C_6H_5)_3Ge[SP(S)(OCH_3)_2]$; see ref. 12. [c] Fluorescence too large to allow for assignment.

TABLE 7

ELECTRON IMPACT (= a) OR FIELD IONIZATION (= b) MASS SPECTRA OF COMPOUNDS 1–10

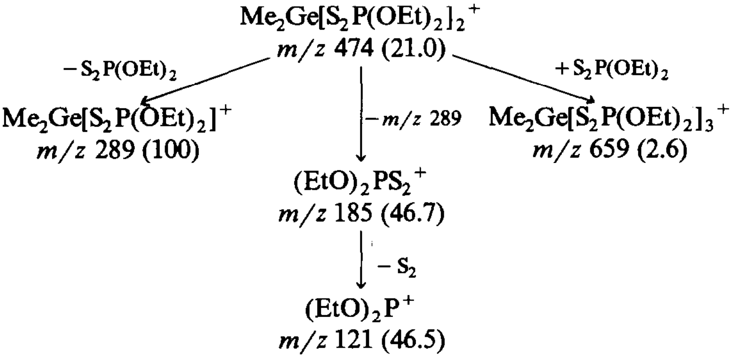
10 ^{a}	**1** ^{b}	**2** ^{a}	**3** ^{a}	**4** ^{b}	**5** ^{b}	**6** ^{b}	**7** ^{b}	**8** ^{b}	**9** ^{b}	Assignment
					659(2.6)					$(CH_3)_2Ge[S_2P(OC_2H_5)_2]_3^{+}$
625.(1.3)										$C_6H_6Ge[S_2P(OCH_3)_2]_3^{+\cdot}$
					555(2.7)	555(6.7)				$[(C_2H_5O)_2PS_2]_3^{+}$
									521(4.5)	$C_6H_5Ge[S_2P(OC_2H_5)_2]_2^{+}$
							490(100)			$(C_6H_5)_3Ge[S_2P(OC_2H_5)_2]^{+\cdot}$
					489(20.4)					$(CH_3)_3Ge[S_2P(OC_2H_5)_2]_2^{+\cdot}$
						474(21.0)				$(CH_3)_2Ge[S_2P(OC_2H_5)_2]_2^{+\cdot}$
468(25.1)										$C_6H_5Ge[Se_2P(OCH_3)_2]_2^{+}$
						459(< 1)				$CH_3Ge[S_2P(OC_2H_5)_2]_2^{+}$
								413(58.0)		$(C_6H_5)_2Ge[S_2P(OC_2H_5)_2]^{+}$
			403(10.0)							$CH_3Ge[S_2P(OCH_3)_2]_2^{+}$
				370(17.3)	370(19.1)		370(3.3)	370(20.0)		$[(C_2H_5O)_2PS_2]_2^{+\cdot}$
								338(38.3)		$[(C_2H_5O)_2PS]_2S^{+\cdot}$
	314(12.3)		314(9.8)							$[(CH_3O)_2PS_2]_2^{+\cdot}$
							306(46.7)			$[(C_2H_5O)_2PS]_2^{+\cdot}$

				304(98.7)						$(CH_3)_3Ge[S_2P(OC_2H_5)_2]^{+\cdot}$
					289(100)					$(CH_3)_2Ge[S_2P(OC_2H_5)_2]^{+}$
	276(100)									$(CH_3)_3Ge[S_2P(OCH_3)_2]^{+\cdot}$
		261(100)								$(CH_3)_2Ge[S_2P(OCH_3)_2]^{+}$
									260(72.3)	$HGe[S_2P(OC_2H_5)_2]^{+\cdot}$
231(13.1)			231(9.8)							$Ge[S_2P(OCH_3)_2]^{+}$
								214(100)		$(C_2H_5O)_2PS_2C_2H_5{}^{+\cdot}$
203(21.7)										$Ge[S_2P(OH)_2]^{+}$
						186(100)			186(100)	$(C_2H_5O)_2PS_2H^{+\cdot}$
				185(36.2)	185(46.7)	185(83.0)	185(10.5)	185(64.3)		$(C_2H_5O)_2PS_2{}^{+}$
172(27.9)										$(CH_3O)_2PS_2CH_3{}^{+\cdot}$
158(6.4)		158(6.1)	158(60.8)							$(CH_3O)_2PS_2H^{+\cdot}$
157(8.1)	157(7.5)	157(4.4)								$(CH_3O)_2PS_2{}^{+}$
				153(4.6)	153(12.7)			153(15.9)		$(C_2H_5O)_2PS^{+\cdot}$
151(4.4)										$C_6H_5Ge^{+}$
		136(17.6)								$(CH_3)_2GeS^{+\cdot}$
125(100)		125(39.4)	125(100)							$(CH_3O)_2PS^{+}$
				121(100)	121(46.5)					$(C_2H_5O)_2P^{+}$
	119(<1)									$(CH_3)_3Ge^{+}$
93(91.0)		93(35.5)	93(45.3)							$(CH_3O)_2P^{+}$

spectra again indicates that all compounds have the same basic tetrahedral environment about Ge with monodentate linkages.

Mass spectra

The mass spectral data of the dithiophosphate compounds are presented in Table 7 for the electron impact and field ionization modes. The fragmentation patterns of the compounds are relatively simple and may be compared to halomethyl and halophenylgermanes [25], and analogous tin dithiophosphates [26,27]. The germanium containing clusters are readily recognizable by their distinct isotope pattern. Representative fragmentations are shown in Scheme 1.



SCHEME 1

Molecular ions are not seen for some compounds even in the FI mode. However, in the FI spectra of trimethyl(*O,O'*-dimethyldithiophosphato)germanium (**1**), trimethyl(*O,O'*-diethyldithiophosphato)germanium (**4**) and triphenyl(*O,O'*-diethyldithiophosphato)germanium (**7**), the M^+ ions dominate the spectra. The formation of free acid peaks at m/z 158 and m/z 186 and their oligomers are evident in all compounds, but no peaks higher than the molecular ion that contain germanium are observed with the exception of $Me_2Ge[S_2P(OEt)_2]_3^+$. The reports on tin dithiophosphate derivatives [26,27] specifically stated that no peaks higher than the molecular ion were observed, thus excluding the possibility of association in the gas phase. The compounds display a clear preference to form clusters corresponding to $[M-L]^+$ fragments over $[M-CH_3]^+$ or $[M-C_6H_5]^+$ fragments. Thus it again seems reasonable to assume that the germanium atom is linked by only one sulfur atom and the molecules possess monodentate dithiophosphate groups.

Acknowledgement

We thank the NSERC – Strategic Grants Program – Industrial Materials and Processes for financial support.

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