3886 *Inorg. Chem.* **1994**, *33*, 3886-3892

Syntheses and Structures of Germanium(II) and Germanium(IV) Thiolate and Selenolate Complexes: $[Et_4N][Ge(SPh)_3]$, $[Ph_4P][Ge(SePh)_3]$, $[Ph_4P]_2[Ge_2(SCH_2CH_2S)_3]$, $Ge(S\text{-}4\text{-}MeC_6H_4)_4$, and $Ge(Se\text{-}2,4,6\text{-}Me_3C_6H_2)_4$. Examples of the First Anionic Germanium(II) Complexes Containing the Trigonal Pyramidal $Ge^{II}S_3$ and $Ge^{II}Se_3$ Cores

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Received March 2, 1994[⊗]

A series of germanium(II) thiolato and selenolato complexes were prepared by metathesis reactions of germanium dibromide with the sodium salts of benzenethiol, benzeneselenol, and ethanedithiol in mixed diethyl ether–methanol solutions. The crystalline products $[Et_4N][Ge(SPh)_3]$ (**1**), $[Ph_4P][Ge(SePh)_3]$ (**2**), and $[Ph_4P]_2[Ge_2(SCH_2CH_2S)_3]$ (**3**) contain the first anionic germanium(II) complexes featuring trigonal pyramidal $Ge^{II}S_3$ or $Ge^{II}Se_3$ cores, and all were structurally characterized by X-ray crystallography. Both **1** and **2** crystallize from hot methanol or acetonitrile in the monoclinic space group $P2_1/c$ with unit cell dimensions $a = 18.374(4)$ Å, $b = 9.052(2)$ Å, $c = 17.595(4)$ Å, $\beta = 113.04(3)°$, $V = 2693$ Å^3, and $Z = 4$ for **1** and $a = 10.665(3)$ Å, $b = 17.204(4)$ Å, $c = 20.345(6)$ Å, $\beta = 105.34(2)°$, $Z = 4$, and $V = 3616$ Å^3 for **2**. The dinuclear complex **3** crystallizes from hot methanol in the triclinic space group $P\bar{1}$ with $a = 9.593(2)$ Å, $b = 10.232(2)$ Å, $c = 13.880(3)$ Å, $\alpha = 105.78(2)°$, $\beta = 91.90(2)°$, $\gamma = 106.62(2)°$, $Z = 1$, and $V = 1247$ Å^3. The molecular anions of **1–3** contain stereochemically active Ge lone pairs, and bond angles at germanium are 87.6(1)–102.2(1)° (for **1** and **2**) and 90.1(1)–100.9(1)° (for **3**). The tetrahedrally coordinated germanium(IV) derivatives $Ge(S\text{-}4\text{-}MeC_6H_4)_4$ (**4**) and $Ge(Se\text{-}2,4,6\text{-}Me_3C_6H_2)_4$ (**5**) were also synthesized and structurally characterized: Orthorhombic **4** crystallizes in the space group $Pbca$ with $a = 16.660(2)$ Å, $b = 16.325(3)$ Å, $c = 19.962(3)$ Å, $V = 5429$ Å^3, and $Z = 8$. **5** forms monoclinic crystals (space group $P2_1/n$) with $a = 12.627(4)$ Å, $b = 21.803(6)$ Å, $c = 13.119(4)$ Å, $\beta = 106.16(2)°$, $V = 3469$ Å^3, and $Z = 4$. The mononuclear complexes with tetrahedrally coordinated germanium(IV) show slight distortions from ideal T_d symmetry. The germanium(II) and germanium(IV) complexes are characterized by infrared and Raman spectroscopy.

Introduction

Some recent work in this laboratory has focused on the synthesis and characterization of novel thiolate and selenolate complexes that involve heavier group 13 (Tl) and group 14 elements (Pb, Sn) of lower valencies.[1-3] Our interest in the chemistry of heavier main group metal thiolates and selenolates has arisen largely from their utility as potential "single-source" precursors to binary III–VI or IV–VI semiconductor materials.[4-6] While there is an intense search for alternative precursors for II–IV semiconductor materials,[7] new sources for III–VI or IV–VI materials are only now beginning to be developed.[8] Moreover, the use of complexes of subvalent group 13 or group 14 elements is of further interest because they contain a site of latent reactivity, the lone pair, which may react with other organometallic moieties to form heterobimetallic species of fixed stoichiometry.[9] In the course of this work, we have now concentrated our attention on the development of low molecular mass anionic thiolate and selenolate complexes of divalent germanium that might serve as possible precursors for the production of small band gap chalcogenide surface films.

While germanium(IV) chalcogenide and chalcogenolate compounds have come under increased investigation in the past several years,[10] it is somewhat surprising that there have been relatively few studies of the analogous chemistry of divalent germanium. However, some compounds of the type $Ge(SR)_2$ (SR = thiolate ligand)[11,12] or $Ge(S_2P(Me)_2)$[13] have been reported. Very recently a monomeric selenogermylene has been reported which is stabilized by coordination of the 4s lone pair of germanium by a transition metal acceptor.[14] In contrast, trigonal pyramidal thiolate or selenolate complexes of the type $[Ge(SR)_3]^-$ or $[Ge(SeR)_3]^-$ have not been characterized yet.

[⊗] Abstract published in *Advance ACS Abstracts*, August 1, 1994.

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0020-1669/94/1333-3886$04.50/0

In attempts toward the synthesis of novel germanium(II) complexes with thiolate and selenolate ligands, we were successful in obtaining three such complexes employing germanium dibromide as a starting agent. We report here the syntheses and the structures of the first germanium(II) thiolate and selenolate complexes with trigonal pyramidal $Ge^{II}S_3$ and $Ge^{II}Se_3$ cores. We further present the crystal structures of two germanium(IV) complexes with thiolate and selenolate ligands as well as their infrared and Raman spectra.

Experimental Section

$GeBr_2$,[15] $GeBr_4$,[15] benzeneselenol,[16] and 2,4,6-trimethylbenzeneselenol[16] (mesityleneselenol) were prepared according to published procedures. Germanium was a gift from Preussag AG. All other reagents were obtained commercially. All manipulations were carried out under a dry atmosphere of nitrogen employing standard Schlenk techniques or a glovebox. The solvents MeOH, Et_2O, and MeCN (Merck) were predried over molecular sieves and freshly distilled from appropriate drying agents.

Preparation of Germanium(II) Compounds. Complexes **1**–**3** were prepared by metathesis reactions of the sodium salts of benzenethiol, benzeneselenol, or ethanedithiol with germanium dibromide at room temperature. In a typical reaction, solutions containing 9 mmol of the deprotonated ligands in 10 mL of methanol were added dropwise to a stirred solution of germanium dibromide (0.700 g, 3 mmol (for **1** and **2**); 1.39 g, 6 mmol (for **3**)) in 15 mL of diethyl ether. The resulting solutions were stirred for 5 min and then were filtered. After addition of solutions of Et_4NBr (0.63 g, 3 mmol (for **1**)) or Ph_4PBr (1.260 g, 3 mmol (for **2**); and 2.520 g, 6 mmol (for **3**)) in 5 mL of methanol, **1**–**3** deposited as microcrystalline products. Crystals suitable for single-crystal X-ray structure determination were obtained by recrystallization from methanol (**1**, **3**) or acetonitrile (**2**).

$[Et_4N][Ge(SPh)_3]$ (1). The crude product was purified by recrystallization from methanol: colorless plates; yield 1.24 g (78%); mp 82 °C dec. Anal. Calcd for $C_{26}H_{35}NGeS_3$: C, 58.88; H, 6.65; N, 2.64. Found: C, 58.79; H, 6.83; N, 2.74.

$[Ph_4P][Ge(SePh)_3]$ (2). The crude product was purified by recrystallization from acetonitrile: yellow cubes; yield 1.72 g (65%); mp 173–174 °C dec. Anal. Calcd for $C_{42}H_{35}GePSe_3$: C, 57.31; H, 4.01. Found: C, 57.20; H, 4.12.

$[Ph_4P]_2[Ge_2(SCH_2CH_2S)_3]$ (3). During the addition of the ligand, a yellow precipitate formed as an intermediate which disappeared when addition was complete. The light yellow solution was stirred for 5 min and then was filtered. The crude product was purified by recrystallization from methanol: yellow cubes; yield 2.24 g (68%); mp 148–150 °C dec. Anal. Calcd for $C_{54}H_{52}P_2Ge_2S_6$: C, 58.39; H, 4.76. Found: C, 58.81; H, 4.64.

Preparation of Germanium(IV) Compounds. $Ge(S\text{-}4\text{-}MeC_6H_4)_4$ (4). This compound was prepared according to the procedure described in ref 17. The crude solid was recrystallized from toluene to give **4** as white needles in 88% yield (1.00 g); mp 110 °C. Anal. Calcd for $C_{28}H_{28}GeS_4$: C, 59.48; H, 4.99. Found: C, 59.30; H, 4.92. MS: *m/e* 566 (M^+, 18) 443 ($M^+ - (SR)$, 20), 320 ($M^+ - (SR)_2$, 15), 197 ($M^+ - (SR)_3$, 46) (R = C_6H_4-4-Me).

$Ge(Se\text{-}2,4,6\text{-}Me_3C_6H_2)_4$ (5). A solution containing 8 mmol of NaSe-2,4,6-$Me_3C_6H_2$ in 20 mL of methanol was added dropwise to tetrabromogermane (0.780 g, 2 mmol) at 0 °C. After evaporation of the solvent under reduced pressure, the yellow powder **5** was extracted in 20 mL of toluene, and the extract was filtered. Orange-yellow needles deposited from the solution upon standing for 2–3 days at 0 °C: yield 1.49 g (86%); mp 211 °C. Anal. Calcd for $C_{36}H_{44}GeSe_4$: C, 49.98; H, 5.13. Found: C, 50.30; H, 5.02. MS: *m/e* 870 (M^+, 10), 671 ($M^+ - (SR)$, 10), 472 ($M^+ - (SR)_2$, 8), 273 ($M^+ - (SR)_3$, 36) (R = C_6H_2-2,4,6-Me_3).

Physical Measurements. Melting points were obtained using a Mettler melting point apparatus (FP 51) and are uncorrected. All elemental analyses were performed on a Hewlett Packard Scientific Model 185. The infrared spectra were recorded on a Bruker IF 113v spectrometer as polyethylene pellets. The Raman spectra were recorded on a Bruker IFS 66 spectrometer using the 1064-nm exciting line of a Neodym YAG laser with samples sealed in capillary tubes. Mass spectra were obtained by means of a Finnigan MAT CH5 mass spectrometer at 70 eV and are reported as *m/e* (ion percent relative intensity). In the case of isotope patterns, the value given is for the most intense peak.

Table 1. Crystallographic Data for $[Et_4N][Ge(SPh)_3]$ (**1**), $[Ph_4P][Ge(SePh)_3]$ (**2**), and $[Ph_4P]_2[Ge_2(SCH_2CH_2S)_3]$ (**3**)

	1	**2**	**3**
formula	$C_{26}H_{35}NGeS_3$	$C_{42}H_{35}GePSe_3$	$C_{54}H_{52}Ge_2P_2S_6$
fw	530.32	880.14	1100.44
cryst dimens, mm^3	0.35 × 0.35 × 0.08	0.20 × 0.15 × 0.12	0.22 × 0.17 × 0.25
T, K	253	170	150
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a, Å	18.374(4)	10.665(3)	9.593(2)
b, Å	9.052(2)	17.204(4)	10.232(2)
c, Å	17.595(4)	20.345(6)	13.880(3)
α, deg			105.78(2)
β, deg	113.04(3)	105.34(2)	91.90(2)
γ, deg			106.62(2)
V, $Å^3$	2693	3616	1247
Z	4	4	1
D_{calcd}, g cm^{-3}	1.31	1.62	1.47
μ(Mo Kα), mm^{-1}	1.38	3.94	1.56
transm factors	0.92–0.68	0.53–0.39	0.75–0.61
scan type	ω–2θ	ω	ω–2θ
2θ range, deg	4–52	5–54	4–54
reflcns	$\pm h,k,l$	$h,k,\pm l$	$h,\pm k,\pm l$
tot. no. of reflcns	5819	8678	5865
tot. no. of unique data	5279	7780	5777
no. of data, $I > 2\sigma(I)$	3100	3971	4925
no. of params refined	272	431	325
R^a (R_w),^{b} %	5.42 (5.24)	4.31 (3.73)	3.18 (3.64)
goodness of fit	1.903	1.186	1.69

[a] $R = (\sum||F_o| - |F_c||)/\sum|F_o|$. [b] $R_w = [(\sum w(|F_o| - |F_c|)^2)/(\sum wF_o^2)]^{1/2}$; $1/w = \sigma^2(F_{hkl}) + 0.0001|F_{hkl}|^2$; $\sigma(F_{hkl}) = \sigma(I)/(2|F_{hkl}|Lp)$.

X-ray Structure Determination Procedures. Crystal data together with data collection and refinement parameters for the structures reported are summarized in Tables 1 and 6. Single crystals of suitable dimensions were epoxied to glass fibers and were mounted on an Enraf-Nonius CAD 4 (for **1**) or Siemens R3 diffractometer (for **2**–**5**). Graphite-monochromated Mo Kα X-radiation (λ = 0.710 73 Å) was used throughout. Cell constants and orientation matrices were determined by least-squares refinements to the setting parameters of 25 (for **1** and **3**), 18 (for **2** and **4**), and 23 (for **5**) reflections. Intensity data were collected using the ω–2θ scan (for **1** and **3**) or ω-scan technique (for **2**, **4**, and **5**). Two (for **2**–**5**) or three (for **1**) standard reflections were measured every 98 reflections, and the data were scaled accordingly and corrected for Lorentz and polarization effects. The corrections for absorption (ψ-scan technique) were applied to the intensity data for all complexes, which resulted in transmission factors in the ranges 0.92–0.68 (for **1**), 0.53–0.39 (for **2**), 0.75–0.61 (for **3**), 0.77–0.59 (for **4**), and 0.42–0.31 (for **5**).

Each crystal structure was solved using direct methods with full-matrix least-squares refinement, employing the SHELXTL PLUS[18a] program package (Siemens Analytical X-ray Instruments Inc., 1992). The remaining non-hydrogen atoms were located by subsequent difference Fourier maps and least-squares refinements. Neutral-atom scattering factors were taken from ref 18b. The methylene carbon atoms (C(41), C(51), C(61), and C(71)) of the $[Et_4N]^+$ cation of **1** and the methylene carbon atom C(3) of **3** are disordered. The multiplicities of these carbon atoms were refined as follows: C(41), C(51), C(61), C(71) 0.748(7) and C(41a), C(51a), C(61a), C(71a) 0.252(7), for **1**; C(3a) 0.67(1) and C(3b) 0.33(1), for **3**. Anisotropic temperature factors were used for all refined atoms except for methyl and methylene carbon atoms of the $[Et_4N]^+$ cation of **1**. After anisotropic refinement, the positions of hydrogen atoms were calculated (d(C–H) = 0.96 Å) and were refined using a riding model with isotropic thermal parameters fixed at 0.08 $Å^2$ (for **1**) or fixed at 1.2 times the equivalent isotropic U of the atom to which they were bonded (for **3**–**5**). The isotropic thermal parameters of the hydrogen atoms, for **2**, were refined. No hydrogen atoms were added to the carbon atoms C(41A), C(51A), C(61A), and C(71A) for **1**.

The final atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Tables 2–4, 7, and 8. Additional crystallographic data are available as supplementary material.

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Table 2. Final Positional and Isotropic Thermal Parameters (Å^2) for the Anions in $[Et_4N][Ge(SPh)_3]$ (**1**)

atom	*x*	*y*	*z*	U_{eq}[a]
Ge	0.31843(4)	0.08203(7)	0.29088(4)	0.0463(3)
S(1)	0.42539(9)	0.17474(22)	0.40214(10)	0.0662(9)
S(2)	0.26086(10)	0.01853(18)	0.38556(9)	0.0571(9)
S(3)	0.26554(9)	0.32113(17)	0.24692(10)	0.0543(7)
C(11)	0.4982(3)	0.1664(7)	0.3600(3)	0.045(3)
C(12)	0.5586(3)	0.0656(6)	0.3903(4)	0.053(3)
C(13)	0.6165(4)	0.0573(7)	0.3595(4)	0.065(4)
C(14)	0.6153(4)	0.1504(9)	0.2980(4)	0.072(4)
C(15)	0.5569(4)	0.2532(9)	0.2678(4)	0.073(4)
C(16)	0.4975(4)	0.2628(7)	0.2988(4)	0.062(3)
C(21)	0.1808(3)	–0.0943(6)	0.3258(3)	0.046(3)
C(22)	0.1111(4)	–0.0861(8)	0.3380(4)	0.071(4)
C(23)	0.0485(5)	–0.175(1)	0.2954(6)	0.102(5)
C(24)	0.0534(6)	–0.2757(10)	0.2387(6)	0.104(5)
C(25)	0.1217(5)	–0.2854(8)	0.2261(4)	0.082(4)
C(26)	0.1857(4)	–0.1961(7)	0.2688(4)	0.058(3)
C(31)	0.1772(3)	0.2872(6)	0.1610(3)	0.044(3)
C(32)	0.1531(4)	0.3831(7)	0.0943(4)	0.067(4)
C(33)	0.0826(4)	0.3620(9)	0.0275(4)	0.081(4)
C(34)	0.0353(4)	0.2438(9)	0.0241(4)	0.080(4)
C(35)	0.0588(4)	0.1463(8)	0.0892(4)	0.067(3)
C(36)	0.1279(3)	0.1695(7)	0.1570(4)	0.053(3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Final Positional and Isotropic Thermal Parameters (Å^2) for the Anions in $[Ph_4P][Ge(SePh)_3]$ (**2**)

atom	*x*	*y*	*z*	U_{eq}[a]
Ge	0.16141(7)	0.22395(5)	–0.09169(3)	0.0255(3)
Se(1)	0.12085(7)	0.28353(5)	0.01117(3)	0.0327(3)
Se(2)	0.31723(7)	0.33140(4)	–0.09552(3)	0.0284(3)
Se(3)	0.31196(8)	0.12937(4)	–0.01931(4)	0.0317(3)
C(11)	–0.0624(6)	0.2660(4)	–0.0052(3)	0.023(3)
C(12)	–0.1424(6)	0.3268(4)	0.0009(3)	0.025(3)
C(13)	–0.2741(7)	0.3150(5)	–0.0079(3)	0.035(3)
C(14)	–0.3274(7)	0.2422(5)	–0.0228(4)	0.041(4)
C(15)	–0.2480(8)	0.1813(5)	–0.0299(4)	0.044(4)
C(16)	–0.1187(7)	0.1925(4)	–0.0227(3)	0.032(3)
C(21)	0.3303(7)	0.3154(4)	–0.1866(3)	0.022(3)
C(22)	0.4506(7)	0.3036(4)	–0.1983(3)	0.031(3)
C(23)	0.4605(7)	0.2943(4)	–0.2649(3)	0.035(3)
C(24)	0.3477(8)	0.2945(4)	–0.3189(4)	0.037(3)
C(25)	0.2295(8)	0.3073(4)	–0.3066(3)	0.037(3)
C(26)	0.2197(7)	0.3175(4)	–0.2409(3)	0.033(3)
C(31)	0.3583(6)	0.0707(4)	–0.0901(3)	0.029(3)
C(32)	0.3831(7)	–0.0082(4)	–0.0821(4)	0.034(3)
C(33)	0.4148(7)	–0.0497(4)	–0.1330(4)	0.039(3)
C(34)	0.4216(6)	–0.0149(5)	–0.1921(4)	0.033(3)
C(35)	0.3997(7)	0.0635(5)	–0.2003(4)	0.042(4)
C(36)	0.3688(6)	0.1071(4)	–0.1494(3)	0.031(3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Final Positional and Isotropic Thermal Parameters (Å^2) for the Anions in $[Ph_4P]_2[Ge_2(SCH_2CH_2S)_3]$ (3)

atom	*x*	*y*	*z*	U_{eq}[a]
Ge	0.11301(3)	0.39262(3)	0.77889(2)	0.0237(1)
S(1)	0.04807(7)	0.16418(6)	0.66305(5)	0.0260(3)
S(2)	0.07733(7)	0.48804(6)	0.64954(5)	0.0269(3)
S(3)	–0.11212(6)	0.36977(7)	0.84493(4)	0.0254(2)
C(1)	0.0218(4)	0.2049(3)	0.5451(2)	0.039(1)
C(2)	–0.0394(3)	0.3277(3)	0.5579(2)	0.035(1)
C(3a)	–0.0465(4)	0.5146(4)	0.9625(3)	0.028(2)[b]
C(3b)	–0.0410(7)	0.4206(7)	0.9798(5)	0.017(3)[b]

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] Site occupancies: C(3a), 0.67 (1); C(3b), 0.33(1).

Results

Syntheses. Complexes **1** and **2** were synthesized according to reaction 1. The neutral compounds $Ge(SPh)_2$ or $Ge(SePh)_2$ which were formed during the reaction appeared to be soluble in mixed diethyl ether–methanol solutions. This is in contrast to the properties of neutral thiolates or selenolates of divalent tin or lead, which are insoluble in all common solvents due to the formation of coordination polymers.[19,20]

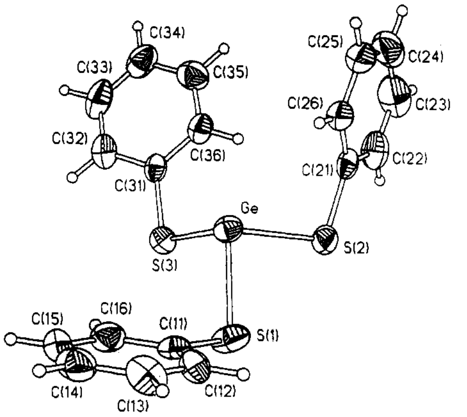

Figure 1. Structure and atomic numbering of the anion in $[Et_4N][Ge(SPh)_3]$ (**1**; 50% probability thermal ellipsoids).

$$GeBr_2 + 3NaEPh \rightarrow NaGe[EPh]_3 + 2NaBr \quad (E = S, Se) \tag{1}$$

$$2GeBr_2 + 3NaSCH_2CH_2SNa \rightarrow Na_2[Ge_2(SCH_2CH_2S)_3] + 4NaBr \tag{2}$$

The yellow precipitate which was formed as an intermediate in the preparation of **3** (reaction 2) was identified as $Ge(SCH_2CH_2S)$ by elemental analysis. However, attempts to crystallize this neutral germanium(II) thiolate complex were unsuccessful. As was expected, $Ge(SCH_2CH_2S)$ reacts readily with further ethanedithiolate to form the anion of **3**. All anions were isolated as their $[Et_4N]^+$ or $[Ph_4P]^+$ salts.

Structural Descriptions. (a) $[Et_4N][Ge(SPh)_3]$ (1) and $[Ph_4P][Ge(SePh)_3]$ (2). The crystal structures of **1** and **2** consist of well-separated cations and anions. The structures of the cations are unexceptional and are not further considered. **2** is isomorphous and isostructural with $[AsPh_4][M(EPh)_3]$ (M = Sn(II), Pb(II); E = S, Se).[19,20]

The molecular structure of the anion of **1** with the atomic numbering scheme is shown in Figure 1, with pertinent bond lengths and angles given in Table 5. A stereoview of **2** with the atomic numbering scheme is shown in Figure 2. Both $[GeE_3]$ units (E = S, Se) are distorted trigonal pyramidal with stereochemically active Ge lone pairs. There are two sets of individual E–Ge–E angles. The angles E(1)–Ge–E(2) and E(1)–Ge–E(3) are nearly equal and close to 90°, while the third one, E(2)–Ge–E(3), is close to 100°. These deviations in E–Ge–E angles result from the steric interactions between the phenyl substituents in the solid state. The large angle correlates with short intramolecular nonbonded distances between hydrogen (H(36)) and carbon atoms (C(21) and C(26), for **1**; C(21) and C(22), for **2**): 2.67 and 2.93 Å, respectively, in **1**; 2.71 and 2.87 Å, respectively, in **2**. The average Ge–S and Ge–Se bond lengths are 2.355 and 2.486 Å, respectively. In essence, the molecular structures of both anions show only slight differences; the most notable deviation being in the conformations of the SPh and SePh ligands.

(b) Structure of $[Ph_4P]_2[Ge_2(SCH_2CH_2S)_3]$ (3). **3** crystallizes in the triclinic space group $P\bar{1}$. The unit cell contains one centrosymmetrically related dinuclear anion and a pair of centrosymmetrically related $[Ph_4P]^+$ cations, with all atoms occupying general positions (Table 4). A view of the anion of

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Table 5. Selected Bond Lengths (Å) and Angles (deg) for **1–3**

	Bond Lengths for **1**		
Ge–S(1)	2.321(2)	S(1)–C(11)	1.768(7)
Ge–S(2)	2.367(2)	S(2)–C(21)	1.761(5)
Ge–S(3)	2.375(2)	S(3)–C(31)	1.758(5)
	Bond Lengths for **2**		
Ge–Se(1)	2.477(1)	Se(1)–C(11)	1.917(7)
Ge–Se(2)	2.501(1)	Se(2)–C(21)	1.922(7)
Ge–Se(3)	2.481(1)	Se(3)–C(31)	1.932(7)
	Bond Lengths for **3**		
Ge–S(1)	2.344(1)	S(2)–C(2)	1.812(2)
Ge–S(2)	2.323(1)	S(3)–C(3a)	1.828(3)
Ge–S(3)	2.349(1)	S(3)–C(3b)	1.850(6)
S(1)–C(1)	1.823(3)		
	Bond Angles for **1**		
S(1)–Ge–S(2)	87.6(1)	Ge–S(1)–C(11)	99.3(2)
S(1)–Ge–S(3)	92.8(1)	Ge–S(2)–C(21)	102.7(2)
S(2)–Ge–S(3)	102.2(1)	Ge–S(3)–C(31)	104.1(2)
	Bond Angles for **2**		
Se(1)–Ge–Se(2)	89.3(1)	Ge–Se(1)–C(11)	100.7(2)
Se(1)–Ge–Se(3)	89.8(1)	Ge–Se(2)–C(21)	98.3(2)
Se(2)–Ge–Se(3)	100.0(1)	Ge–Se(3)–C(31)	98.6(2)
	Bond Angles for **3**		
S(1)–Ge–S(2)	90.1(1)	Ge–S(3)–C(3b)	97.8(2)
S(1)–Ge–S(3)	97.1(1)	S(1)–C(1)–C(2)	112.5(2)
S(2)–Ge–S(3)	100.9(1)	S(2)–C(2)–C(1)	111.7(2)
Ge–S(1)–C(1)	101.0(1)	S(3)–C(3a)–C(3aa)	114.6(4)
Ge–S(2)–C(2)	99.2(1)	S(3)–C(3b)–C(3ba)	111.5(7)
Ge–S(3)–C(3a)	97.8(1)		

3 is shown in Figure 3. Selected bond lengths and angles for the anion are presented in Table 5.

As can be seen in Figure 3a, two five-membered Ge(SCH_2CH_2S) chelate rings are linked via one ethanedithiolate bridge at the respective Ge(II) sites, with formation of a distorted trigonal pyramidal environment around each germanium atom. The bridging ethanedithiolate ligand has a trans configuration in the solid state. The alternate orientation of the central bridging ligand within the disordered crystal structure is depicted in Figure 3b. The Ge···Ge distance within the dinuclear anion is 6.593 Å. The distorted environment around germanium is most likely due to the fact that one of the ligands is a chelate with a smaller bite angle at germanium (90.1(1)°) as compared to the exocyclic S–Ge–S angles (97.1(1) and 100.9(1)°). The Ge–S bond lengths observed for **3** range from 2.323(1) to 2.349(1) Å. However, the mean Ge–S distance of 2.338(1) Å appears slightly shorter than the corresponding one in **1** (2.355(2) Å).

In the five-membered chelate rings, C(2) is displaced by 0.70 Å from the least-squares plane determined for Ge, S(1), S(2), and C(1) (mean deviation 0.03 Å), giving rise to an envelope conformation.

(c) Ge(S-4-MeC$_6$H$_4$)$_4$ (4) and Ge(Se-2,4,6-Me$_3$C$_6$H$_2$)$_4$ (5). The unit cells of **4** and **5** contain neutral monomeric molecules of Ge(S-4-MeC$_6$H$_4$)$_4$ and Ge(Se-2,4,6-Me$_3$C$_6$H$_2$)$_4$. Perspective drawings of the structures are shown in Figures 4 and 5. Positional parameters of the non-hydrogen atoms and the equivalent values of the anisotropic temperature factors for **4** and **5** are given in Tables 7 and 8, while selected bond lengths and angles are summarized in Table 9.

Both compounds, **4** and **5**, contain four-coordinated Ge(IV) atoms in distorted tetrahedral environments. In **4**, the bond angles at germanium vary from 105.0(1) to 117.4(1)° and those at sulfur from 99.3(1) to 103.7(1)°. The corresponding variations in **5** are from 103.6(1) to 115.4(1)° for germanium and from 99.4(3) to 102.8(1)° for selenium. The average Ge–S and Ge–Se distances are 2.217 and 2.374 Å. The S–C and Se–C distances in **4** and **5** average 1.784 and 1.93 Å. We note that there are short intermolecular Se···Se distances between neighboring molecules of **5** (3.885(2) Å for Se(1)···Se(2a) and Se(1a)···Se(2)), while in **4** the closest nonbonding intermolecular S···S distance is observed at 5.039(2) Å. We attribute these close distances to crsytal packing forces of the more flattened molecules of **5** as compared to **4**. The flattening itself may arise from steric interactions between the *o,o'*-methyl groups of the mesityleneselenol ligands within each molecule of **5**. The most interesting features of compounds **4** and **5** are their monomeric nature and their low molecularity. From their mass spectra it is clearly evident that both compounds contain sufficient volatility and are therefore possible single-source precursors for low-pressure CVD applications.

Infrared and Raman Spectra. Selected frequencies and their assignments for **1–5** are listed in Table 10. For **4** and **5**, infrared and Raman bands (in parentheses) associated with modes of the ligands were located by comparison with the infrared and Raman spectra of Pb(S-4-MeC$_6$H$_4$)$_2$ and Pb(S-2,4,6-Me$_3$C$_6$H$_2$)$_2$.[8c,21] The bands associated with Ge–S and Ge–Se stretching vibrations for **4** and **5**, respectively, are close to Ge–E (E = S, Se) stretching modes observed for other Ge(SR)$_4$[22] or Ge(SeR)$_4$[23] derivatives. The splitting of $\nu_3(F_2)$ is probably caused by an intrinsic distortion of the GeE$_4$ core from T_d symmetry rather than by intermolecular interactions in the solid state.

In contrast, Ge–S or Ge–Se stretching vibrations for **1–3** occur below these values. For **1**, two bands at 345 (339) and 237 (237) cm^{-1} can be readily assigned to the symmetric and antisymmetric stretching vibrations which should be both infrared and Raman active while the bands at 276 (276) and 184 (185) cm^{-1} are associated with vibrations of the ligand.[24] For comparison, Ge–Cl stretching vibrations have been reported to occur at 320 and 253 cm^{-1} for GeCl$_3^-$ anions in aqueous hydrochloric solution.[25] For **2**, various bands in the region 310–250 cm^{-1} are associated with vibrations of the cation and the coordinated ligand SePh$^-$. The Ge–Se stretching vibrations are shifted to 220 and 180 cm^{-1}, reflecting a substantial decrease in the Ge–Se stretching frequency. Tchakirian and Volkringer gave the positions of Ge–Br stretching vibrations for GeBr$_3^-$ as 232 and 200 cm^{-1}.[26] A further comparison of the infrared and Raman spectra of the isoelectronic pairs AsCl$_3$ and AsBr$_3$ provides strong support for this assignment.[27] For each pair, the spectra of the anions of **1** and **2** and the isoelectronic molecules are analogous, each of the frequencies of AsE$_3$ being higher than the corresponding one in [Ge(SR)$_3$]$^-$ or [Ge(SeR)$_3$]$^-$. This is in accordance with expectation, since passage from GeE$_3$ to AsE$_3$ is associated with an increase of the nuclear charge of the metal atom, causing a tightening of the respective bonds.

The three bands to be expected for the Ge–S vibrations of **3** are observed in both the infrared and the Raman spectra at 331 (331), 295 (297), and 241 (236) cm^{-1}. The pattern of bands is much like that of isoelectronic [(CH$_2$S)$_2$AsCl][28] or isostructural [Ph$_4$P]$_2$[Sn$_2$(SCH$_2$CH$_2$)$_3$].[29] Compared to that of [(CH$_2$S)$_2$AsCl], the pattern is shifted by ca. 60 cm^{-1} to lower frequencies, and compared to that of [Ph$_4$P]$_2$[Sn$_2$(SCH$_2$CH$_2$)$_3$], a shift of ca. 20 cm^{-1} to higher frequencies is observed, while two of the three significant features are only slightly shifted when compared to the Ge–S stretching vibrations of **1**.

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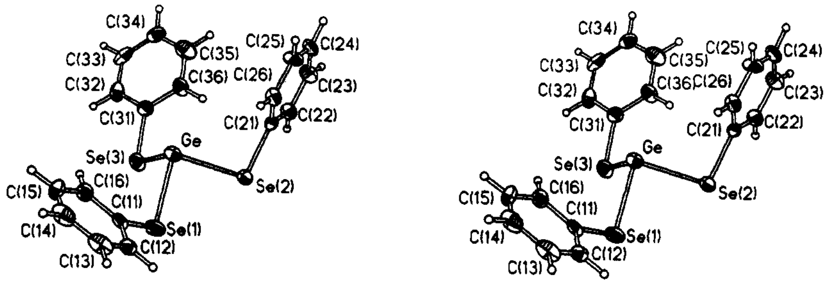

Figure 2. Stereo drawing of the anion in $[Ph_4P][Ge(SePh)_3]$ (**2**; 50% probability thermal ellipsoids).

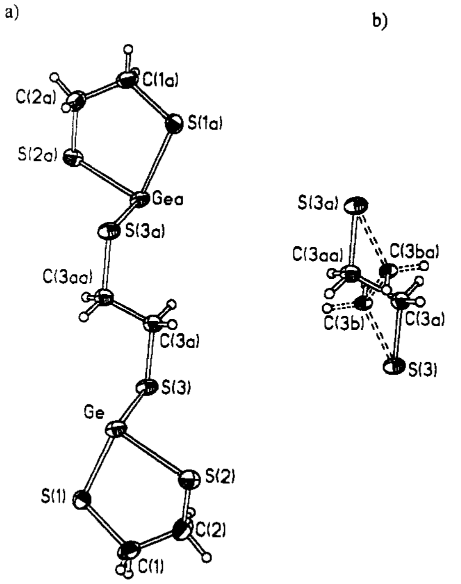

Figure 3. (a) Structure and atomic numbering of the anion in $[Ph_4P]_2[Ge_2(SCH_2CH_2S)_3]$ (**3**; 50% probability thermal ellipsoids). (b) Alternate orientation of the central structural unit within the disordered crystal structure.

Table 6. Crystallographic Data for $Ge(S\text{-}4\text{-}MeC_6H_4)_4$ (**4**) and $Ge(Se\text{-}2,4,6\text{-}Me_3C_6H_2)_4$ (**5**)

	4	**5**
formula	$C_{28}H_{28}GeS_4$	$C_{36}H_{44}GeSe_4$
fw	530.32	880.14
cryst dimens, mm^3	0.18 × 0.50 × 0.25	0.18 × 0.21 × 0.25
T, K	150	150
space group	*Pbca*	$P2_1/n$
a, Å	16.660(2)	12.627(4)
b, Å	16.325(3)	21.803(6)
c, Å	19.962(3)	13.119(4)
β, deg		106.16(2)
V, Å^3	5429	3469
Z	8	4
D_{calcd}, g cm^{-3}	1.39	1.66
μ(Mo Kα), mm^{-1}	1.45	5.10
transm factors	0.77–0.59	0.42–0.31
scan type	ω	ω
2θ range, deg	4–54	4–50
reflcns	h,k,l	$h,k,\pm l$
tot. no. of reflcns	6570	6620
tot. no. of unique data	5879	6090
no. of data, $I > 2\sigma(I)$	3182	2890
no. of params refined	318	390
R^a (R_w),^{b} %	3.67 (3.44)	3.94 (3.63)
goodness of fit	1.063	0.939

^{a} $R = (\sum||F_o| - |F_c||)/\sum|F_o|$. ^{b} $R_w = [(\sum w(|F_o| - |F_c|)^2)/(\sum wF_o^2)]^{1/2}$; $1/w = \sigma^2(F_{hkl}) + 0.0001|F_{hkl}|^2$; $\sigma(F_{hkl}) = \sigma(I)/(2|F_{hkl}|Lp)$.

Discussion

According to the VSEPR model, **1**–**3** are AX_3E type coordination compounds and are thus expected to have a trigonal pyramidal environment around each metal atom. Distorted trigonal arrangements similar to those in **1** and **2** have been observed in the analogous complexes of tin(II) and lead(II) ($[AsPh_4][M(EPh)_3]$: M = Sn, E = S (**1a**); E = Se (**2a**); M = Pb, E = S (**1b**), E = Se (**2b**)).[19,20] While two of the E–M–E angles are nearly equal and close to 90°, the third one (E(2)–M–E(3)) has increased from 96.14(5)° in **1b**, 96.57(4)° in **2b**, 96.73(3)° in **1a**, and 97.27(3)° in **2a** to 102.2(1)° in **1** and 100.0(1)° in **2**. More recently, examples featuring trigonal pyramidal chalcogenide environments were observed for trichalcogenodiplumbate(II) and -distannate(II) anions of the type $[M_2E_3]^{2-}$ (M = Pb, Sn; E = Se, Te).[30]

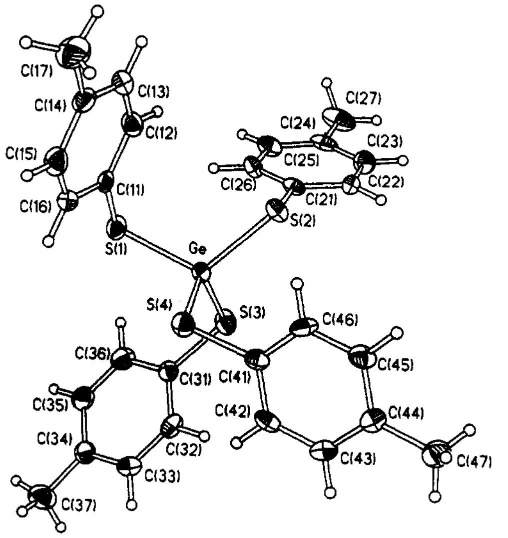

Figure 4. Molecular structure and atomic labeling scheme for **4**. Thermal ellipsoids are plotted at the 50% probability level.

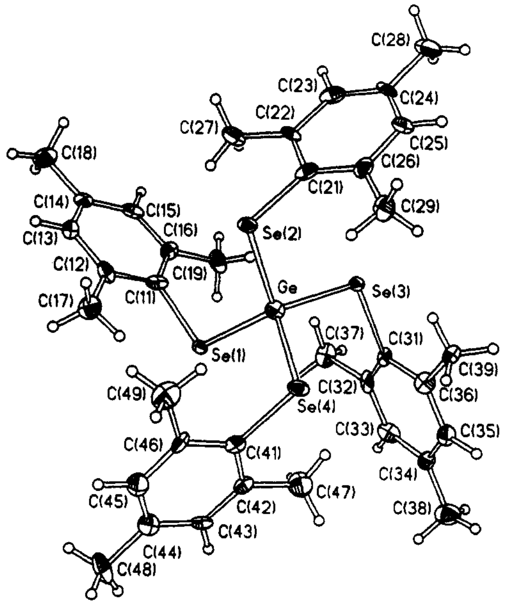

Figure 5. Molecular structure and atomic labeling scheme for **5**. Thermal ellipsoids are plotted at the 50% probability level.

Table 7. Final Positional and Isotropic Thermal Parameters (Å^2) for Ge(S-4-MeC$_6$H$_4$)$_4$ (**4**)

atom	*x*	*y*	*z*	$U_{eq}{}^a$
Ge	0.46555(3)	−0.04493(3)	0.18011(2)	0.0192(2)
S(1)	0.50052(7)	0.06047(7)	0.11611(6)	0.0272(4)
S(2)	0.56542(7)	−0.12907(7)	0.20642(6)	0.0252(4)
S(3)	0.37726(8)	−0.11792(7)	0.12287(6)	0.0292(4)
S(4)	0.42476(7)	0.01054(7)	0.27552(6)	0.0261(4)
C(11)	0.5769(3)	0.1034(3)	0.1675(2)	0.021(2)
C(12)	0.6555(3)	0.0758(3)	0.1633(2)	0.027(2)
C(13)	0.7152(3)	0.1105(3)	0.2023(2)	0.029(2)
C(14)	0.6978(3)	0.1741(3)	0.2474(2)	0.027(2)
C(15)	0.6193(3)	0.2015(3)	0.2506(3)	0.032(2)
C(16)	0.5595(3)	0.1671(3)	0.2119(2)	0.028(2)
C(17)	0.7628(3)	0.2100(3)	0.2912(3)	0.047(2)
C(21)	0.5811(3)	−0.1855(3)	0.1309(2)	0.020(2)
C(22)	0.5910(3)	−0.2698(3)	0.1358(3)	0.028(2)
C(23)	0.6123(3)	−0.3150(3)	0.0804(3)	0.033(2)
C(24)	0.6215(3)	−0.2788(3)	0.0180(2)	0.029(2)
C(25)	0.6086(3)	−0.1952(3)	0.0128(2)	0.029(2)
C(26)	0.5893(3)	−0.1484(3)	0.0686(2)	0.026(2)
C(27)	0.6455(3)	−0.3279(3)	−0.0431(3)	0.046(2)
C(31)	0.2968(2)	−0.0467(3)	0.1138(2)	0.022(2)
C(32)	0.2359(3)	−0.0437(3)	0.1612(2)	0.025(2)
C(33)	0.1699(3)	0.0062(3)	0.1515(2)	0.025(2)
C(34)	0.1624(3)	0.0536(3)	0.0943(2)	0.029(2)
C(35)	0.2236(3)	0.0505(3)	0.0468(2)	0.035(2)
C(36)	0.2904(3)	0.0012(3)	0.0565(2)	0.032(2)
C(37)	0.0879(3)	0.1054(3)	0.0834(3)	0.045(2)
C(41)	0.4017(3)	−0.0758(3)	0.3269(2)	0.022(2)
C(42)	0.3221(3)	−0.1006(3)	0.3349(2)	0.025(2)
C(43)	0.3034(3)	−0.1640(3)	0.3776(2)	0.026(2)
C(44)	0.3619(3)	−0.2045(3)	0.4145(2)	0.024(2)
C(45)	0.4415(3)	−0.1790(3)	0.4061(2)	0.028(2)
C(46)	0.4605(3)	−0.1151(3)	0.3631(2)	0.027(2)
C(47)	0.3411(3)	−0.2722(3)	0.4626(2)	0.034(2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

The ability of germanium(II) complexes to form a highly stable VSEPR type AX$_3$E coordination is further demonstrated by the synthesis and structural characterization of the dinuclear anion of **3**. All attempts to isolate the hypothetical [Ge(SCH$_2$CH$_2$S)$_2$]$^{2-}$ anion were unsuccessful. However, VSEPR type AX$_4$E coordination has been found in a few germanium(II) compounds, including, for example, Ge(S$_2$CNEt$_2$)$_2$ and Ge(S$_2$P(CH$_3$)$_2$).[13] As is expected, the Ge(II)–S or Ge(II)–Se distances observed in **1** (2.355 Å), **2** (2.486 Å), and **3** (2.338 Å) are longer than those observed in the Ge(IV) derivatives **4** (2.217 Å) and **5** (2.374 Å), which compare well with those found for a series of measured Ge(IV)–S and Ge(IV)–Se bond lengths.[10,31,32] The average Ge–S bond length in **1** is only marginally shorter than that in **3**; both may be compared with the average Ge–S bond length of 2.375 Å in [Ge(SC(CH$_3$)$_3$)$_2$]$_2$,[33] although there is considerable variation in the individual Ge–S distances (2.268(3)–2.467(3) Å). The Ge–S$_{eq}$ bond lengths of Ge(S$_2$P(CH$_3$)$_2$)$_2$ were reported to be 2.421(1) and 2.408(1) Å.

A few available structures involving bonds between bivalent germanium and selenium are those of (CO)$_5$WGe(Se-2,4,6-^{t}Bu$_3$C$_6$H$_2$)$_2$ (2.314(2) and 2.346(2) Å)[14] and Ge[C(SePMe$_2$)(PMe$_2$)(SiMe$_3$)]$_2$ (2.769(1) and 2.712(1) Å).[34] In the selenium compound examined here, Ge–Se distances are in the range 2.477(1)–2.501(1) Å.

Concluding Remarks

Stable three-coordinate anionic germanium(II) thiolate and selenolate complexes were prepared for the first time and were shown to be stable under ambient conditions. All examples were characterized in the solid state by single-crystal X-ray diffraction. As compared to four-coordinate Ge(SR)$_4$ and Ge(SeR)$_4$,

Table 8. Final Positional and Isotropic Thermal Parameters (Å^2) for Ge(Se-2,4,6-Me$_3$C$_6$H$_2$)$_4$ (**5**)

atom	*x*	*y*	*z*	$U_{eq}{}^a$
Ge	0.19856(9)	0.29766(5)	0.09311(8)	0.0211(4)
Se(1)	0.06628(10)	0.22435(5)	0.00504(8)	0.0147(4)
Se(2)	0.31515(10)	0.26120(5)	0.25552(8)	0.0184(5)
Se(3)	0.12534(10)	0.39204(5)	0.13415(8)	0.0158(4)
Se(4)	0.30734(10)	0.31381(5)	−0.02685(8)	0.0194(5)
C(11)	0.0431(8)	0.1767(5)	0.1208(8)	0.018(4)
C(12)	0.1000(9)	0.1199(4)	0.1446(8)	0.021(5)
C(13)	0.0761(9)	0.0812(5)	0.2193(8)	0.023(5)
C(14)	−0.0042(9)	0.0958(5)	0.2688(8)	0.020(4)
C(15)	−0.0587(9)	0.1519(5)	0.2451(8)	0.023(5)
C(16)	−0.0350(8)	0.1934(5)	0.1718(8)	0.019(4)
C(17)	0.1875(9)	0.1013(5)	0.0906(8)	0.029(5)
C(18)	−0.0354(9)	0.0525(5)	0.3462(8)	0.029(5)
C(19)	−0.0968(9)	0.2527(4)	0.1474(8)	0.026(5)
C(21)	0.2927(9)	0.3240(5)	0.3505(7)	0.020(4)
C(22)	0.2199(8)	0.3135(5)	0.4132(7)	0.019(4)
C(23)	0.2125(9)	0.3591(5)	0.4851(8)	0.024(5)
C(24)	0.2711(10)	0.4127(5)	0.4989(8)	0.023(5)
C(25)	0.3448(10)	0.4215(5)	0.4380(8)	0.028(5)
C(26)	0.3574(9)	0.3782(4)	0.3632(8)	0.022(5)
C(27)	0.1533(9)	0.2560(4)	0.4037(8)	0.028(5)
C(28)	0.2567(10)	0.4610(5)	0.5767(8)	0.036(5)
C(29)	0.4342(9)	0.3914(5)	0.2991(8)	0.028(5)
C(31)	0.0774(9)	0.4272(4)	−0.0070(8)	0.015(4)
C(32)	−0.0304(9)	0.4181(4)	−0.0706(8)	0.021(5)
C(33)	−0.0627(9)	0.4460(5)	−0.1714(8)	0.023(4)
C(34)	0.0089(10)	0.4813(4)	−0.2090(8)	0.023(5)
C(35)	0.1151(9)	0.4914(4)	−0.1414(8)	0.022(5)
C(36)	0.1482(9)	0.4645(5)	−0.0421(8)	0.021(5)
C(37)	−0.1150(8)	0.3782(4)	−0.0349(8)	0.025(5)
C(38)	−0.0267(10)	0.5091(5)	−0.3172(8)	0.036(5)
C(39)	0.2642(9)	0.4798(4)	0.0265(8)	0.025(5)
C(41)	0.2476(9)	0.2527(5)	−0.1352(8)	0.020(4)
C(42)	0.1582(8)	0.2670(5)	−0.2244(8)	0.019(4)
C(43)	0.1206(9)	0.2244(5)	−0.3005(8)	0.019(4)
C(44)	0.1653(9)	0.1659(5)	−0.2937(8)	0.022(5)
C(45)	0.2506(9)	0.1513(5)	−0.2048(8)	0.027(5)
C(46)	0.2941(9)	0.1938(5)	−0.1236(8)	0.020(4)
C(47)	0.1085(9)	0.3305(5)	−0.2334(8)	0.033(5)
C(48)	0.1230(10)	0.1192(5)	−0.3804(9)	0.035(5)
C(49)	0.3872(9)	0.1751(5)	−0.0285(8)	0.035(5)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 9. Selected Bond Lengths (Å) and Angles (deg) for **4** and **5**

	Bond Lengths for **4**		
Ge–S(1)	2.221(1)	S(1)–C(11)	1.779(4)
Ge–S(2)	2.221(1)	S(2)–C(21)	1.787(4)
Ge–S(3)	2.211(1)	S(3)–C(31)	1.783(4)
Ge–S(4)	2.216(1)	S(4)–C(41)	1.786(4)
	Bond Lengths for **5**		
Ge–Se(1)	2.367(2)	Se(1)–C(11)	1.93(1)
Ge–Se(2)	2.365(2)	Se(2)–C(21)	1.92(1)
Ge–Se(3)	2.378(2)	Se(3)–C(31)	1.939(9)
Ge–Se(4)	2.386(2)	Se(4)–C(41)	1.94(1)
	Bond Angles for **4**		
S(1)–Ge–S(2)	114.8(1)	S(3)–Ge–S(4)	117.4(1)
S(1)–Ge–S(3)	107.1(1)	Ge–S(1)–C(11)	99.3(1)
S(1)–Ge–S(4)	105.0(1)	Ge–S(2)–C(21)	103.2(1)
S(2)–Ge–S(3)	106.7(1)	Ge–S(3)–C(31)	101.6(1)
S(2)–Ge–S(4)	106.2(1)	Ge–S(4)–C(41)	103.7(1)
	Bond Angles for **5**		
Se(1)–Ge–Se(2)	113.0(1)	Se(3)–Ge–Se(4)	110.7(1)
Se(1)–Ge–Se(3)	115.4(1)	Ge–Se(1)–C(11)	102.8(3)
Se(1)–Ge–Se(4)	103.6(1)	Ge–Se(2)–C(21)	100.2(3)
Se(2)–Ge–Se(3)	105.7(1)	Ge–Se(3)–C(31)	99.4(3)
Se(2)–Ge–Se(4)	108.4(1)	Ge–Se(4)–C(41)	101.8(4)

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Table 10. Selected Features and Their Assignments in the Vibrational Spectra of Compounds **1–5**[a]

1			**3**			**2**			**4**			**5**		
IR	Raman	assgnt	IR	Raman	assgnt	IR	Raman	assgnt	IR	Raman	assgnt	IR	Raman	assgnt
366 m	367 w	K							426 s	427 m	ν(Ge–S)$_{\mathrm{asym}}$	341 w	341 w	L
345 s	339 w	ν(Ge–S)$_{\mathrm{sym}}$	331 m	331 m	ν(Ge–S)				412 m	411 w	ν(Ge–S)$_{\mathrm{asym}}$	291 s	295 w	ν(Ge–Se)$_{\mathrm{asym}}$
				323 m					383 m	385 s	L	271 s	270 w	ν(Ge–Se)$_{\mathrm{asym}}$
			312 s						373 w	374 s	L	250 m	251 w	L
			295 s	297 s	ν(Ge–S)	307 vw	307 w	L	354 w	355 m	ν(Ge–S)$_{\mathrm{sym}}$	225 w	225 w	ν(Ge–Se)$_{\mathrm{sym}}$
276 vw	276 vw	L				278 w	281 w	K	302 m	303 w		205 sh		
				265 w	K	260 m	260 sh	K, L		288 m	L	191 m	196 vs	L
			259 m		K	254 m	253 m	K, L	249 vw	249 vw		103 w	100 s	
237 s	237 s	ν(Ge–S)$_{\mathrm{asym}}$	241 m	236 w	ν(Ge–S)				230 vw	230 w				
						220 vw	220 w	ν(Ge–Se)$_{\mathrm{sym}}$	171 w	173 w				
				204 w	K	202 vs	205 m	K	118 w	119 w				
195 m	195 s		194 w	194 sh		185 s								
184 m	185 s	L				175 s	180 m	ν(Ge–Se)$_{\mathrm{asym}}$						
	132 s		145 w	135 s										
	101 vs		116 vw	105 vs			105 vs							

[a] s = strong, m = medium, w = weak, v = very, sh = shoulder; L = vibration of the ligand; K = vibration of the cation.

$[\mathrm{Ge(SR)_3}]^-$ and $[\mathrm{Ge(SeR)_3}]^-$ are much more reactive, making them powerful sources for the preparation of new thiolates or selenolates as possible single-source CVD precursors. Further experiments are in progress to modify these anionic germanium(II) compounds by (a) preparing volatile heterobimetallic compounds in which the germanium s^2 electronic configuration participates in bonding to transition metals, (b) oxidation with elemental sulfur, selenium, and tellurium to prepare neutral mixed chalcogenide/chalcogenolate complexes, and (c) the isolation of neutral $[\mathrm{Ge(ER)_2}]$ compounds upon protonation of anionic $[\mathrm{Ge(ER)_3}]^-$ derivatives.

Acknowledgment is made to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

Supplementary Material Available: For **1–5**, tables of thermal parameters, complete positional parameters, bond angles, and bond distances (17 pages). Ordering information is given on any current masthead page.