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Distortion Coordinate for Nonrigid Five-Coordinated Germanium. Synthesis and Molecular Structure of Spirocyclic Anionic Methylgermanates Varying in Ring Composition[1]

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Reaction of an organogermanium trichloride with a catechol or thiocatechol derivative in the presence of triethylamine, followed by a metathetical exchange, led to the isolation of the Et_4N^+ salts of the five-coordinated spirocyclic germanates $[(C_6H_4O_2)_2GeMe][Et_4N]$ (**1**), $[(MeC_6H_3S_2)_2GeMe][Et_4N]$ (**2**), $[(C_6Cl_4O_2)_2GeMe][Et_4N]$ (**3**), and $[(C_7H_6S_2)_2GePh][Et_4N]$ (**4**). X-ray analysis showed that the geometry of **1** is close to a trigonal bipyramid, **2** is displaced about one-third toward the rectangular pyramid, and **3** is close to the rectangular pyramid. The low structural displacement for **1** is attributed to lattice effects. The structures of **2** and **3** are discussed in terms of ligand effects, the insertion of ring sulfur atoms in **2**, and the electron-withdrawing effect of chlorine ring atoms in **3**. The structures of these and related anionic germanates follow the local C_{2v} constraint of the Berry pseudorotational coordinate with a trans basal angle, θ, for the "limiting" RP of 150.1°, similar to that for other main-group elements in the five-coordinated state. **1** crystallizes in the tetragonal space group $P4_12_12$ with $a = b = 9.834$ (4) Å, $c = 22.275$ (7) Å, and $Z = 4$. **2** crystallizes in the orthorhombic space group *Pbca* with $a = 15.344$ (2) Å, $b = 19.920$ (5) Å, $c = 17.017$ (5) Å, and $Z = 8$. **3** crystallizes in the monoclinic space group $P2_1/c$ with $a = 10.011$ (2) Å, $b = 16.793$ (3) Å, $c = 16.386$ (5) Å, $\beta = 93.78$ (2)°, and $Z = 4$. The final conventional unweighted agreement factors were 0.045 (**1**), 0.065 (**2**), and 0.049 (**3**).

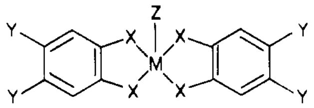
Introduction

Our recent work[2-5] on five-coordinated anionic germanium(IV) complexes centered on derivatives containing a spirocyclic framework with either a hydroxyl or a halogen ligand at the acyclic site. Their X-ray structures,[2-4] which concerned seven derivatives, spanned the range between the two basic geometries for this coordination number, the trigonal bipyramid (TBP) and the square or rectangular pyramid (RP). As with phosphoranes[6-8] and the isoelectronic arsoranes,[9,10] the main criterion in stabilizing the square-pyramidal structure for anionic germanates[2] is the presence of two unsaturated five-membered rings with like atoms in any one ring directly attached to the central atom.

Comparisons of five-coordinated germanium derivatives with more extensively studied elements of main groups 4 (14)[40] and 5 (15)[40] containing a variety of other substituents are limited, however. Here we report the first syntheses and molecular structures of a series of pentacoordinated anionic methylgermanates, **1**–**3**. These compounds contain the same cation, Et_4N^+, but vary in the composition of the spirocyclic system. The thio derivative, $[(C_7H_6S_2)_2GePh][Et_4N]$ (**4**), also was prepared but did not prove amenable to an X-ray investigation. In $[(C_6H_4O_2)_2GeMe][Et_4N]$ (**1**), directly bound oxygen-containing ligands are compared with sulfur-containing ligands in the thio derivative, $[(MeC_6H_3S_2)_2GeMe][Et_4N]$ (**2**). Ring substitution by chlorine atoms in $[(C_6Cl_4O_2)_2GeMe][Et_4N]$ (**3**) allows the determination of the effect of electron-withdrawing substituents on structural displacement.

With this series and a related series containing phenyl substituents at the acyclic site,[11] sufficient examples of pentacoordinated germanates are available to establish the form of the distortion coordinate followed by these nonrigid species and to more fully assess the factors influencing specific geometrical parameters.

Previous conclusions for phosphoranes suggested that in the general representation



the square- or rectangular-pyramidal geometry will be enhanced by electronegative X and Y ligands[6] and the presence of Z groups of increasing steric size.[12] Increasing ring saturation and the incorporation of mixed hetero ring atoms X are expected to lend stability to the trigonal bipyramid.[6,13]

Experimental Section

Proton NMR spectra were recorded on a Varian A-60 spectrometer and are referenced vs. tetramethylsilane. All X-ray crystallographic studies were done by using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated molybdenum radiation ($\lambda(K\alpha_1) = 0.709\,30$ Å, $\lambda(K\alpha_2) = 0.713\,59$ Å) at an ambient temperature of 23 ± 2 °C. Details of the experimental and computational procedures have been described previously.[14]

Syntheses. Tetraethylammonium Bis(1,2-benzenediolato)methylgermanate(IV), $[(C_6H_4O_2)_2GeMe][Et_4N]$ (1). To a vigorously stirred solution of methylgermanium chloride (0.97 g, 5 mmol) in benzene (20 mL) was added dropwise from an addition funnel a solution of catechol (1.1 g, 10 mmol) and triethylamine (2.02 g, 20 mmol) in benzene (150 mL) over a period of 2 h. The progress of the reaction was noted by the occurrence of an exothermic reaction and formation of a curdy white precipitate. The resulting reaction mixture was heated under reflux for 1 h and cooled to room temperature. The precipitate of triethylammonium chloride was removed from the reaction mixture by filtration. Evaporation of solvent from the filtrate gave a colorless viscous liquid, which was dissolved in acetonitrile (20 mL). To this solution was added tetraethylammonium chloride, and the mixture was stirred for 5 min. Evaporation of solvent from the solution afforded a crystalline residue, which was washed with water to dissolve triethylammonium chloride formed as a result of the metathesis reaction and any excess tetraethylammonium chloride. The water-insoluble white precipitate was filtered off under suction and dried in vacuo. Recrystallization of the dried solid from acetonitrile gave white lumpy crystals of tetraethylammonium bis(1,2-benzenediolato)methylgermanate(IV), $[(C_6H_4O_2)_2GeMe][Et_4N]$ (**1**) mp 252–254 °C (yield 2.01 g, 92.6%). ^1H NMR (CD_3CN/Me_4Si) (ppm): 6.55 (m, AA′BB′ pattern, 8 H, protons of catecholate groups); 3.05 (q, 8 H, CH_2 protons of Et_4N^+); 1.10 (m,

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12 H, CH_3 protons of Et_4N^+); 0.6 (s, 3 H, $GeCH_3$). Anal. Calcd for $C_{21}H_{31}O_4NGe$: C, 58.1; H, 7.2; N, 3.23. Found: C, 58.08; H, 7.4; N, 3.24.

Tetraethylammonium Bis(4-methyl-1,2-benzenedithiolato)methylgermanate(IV), $[(C_7H_6S_2)_2GeMe][Et_4N]$ (2). A solution of toluene-3,4-dithiol (0.825 g, 5.26 mmol) and triethylamine (1.07 g, 10.59 mmol) in benzene (70 mL) was added to a vigorously stirred solution of methylgermanium trichloride (0.511 g, 2.63 mmol) at room temperature when a flocculent white precipitate was thrown out of the solution. The resulting reaction mixture was stirred at room temperature for $^1/_4$ h and then heated under reflux for 2 h. Filtration of triethylammonium hydrochloride from the reaction mixture followed by evaporation of the solvent from the filtrate afforded a viscous liquid that solidified upon the addition of acetonitrile (5 mL) and shaking. Addition of a further amount of acetonitrile (20 mL) brought about complete dissolution of the solid. To this solution was added tetraethylammonium chloride (0.44 g, 2.66 mmol), and the mixture was stirred for 5 min. Evaporation of solvent from this reaction mixture in vacuo gave a greenish viscous liquid, which was treated with water, and the suspension was stirred to dissolve $Et_3NH^+Cl^-$ and excess $Et_4N^+Cl^-$. The insoluble viscous mass was separated by decantation of the aqueous layer, dried under oil-pump vacuum, and dissolved in minimum volume of acetone at room temperature to obtain a clear greenish solution. Hexane was added dropwise to this solution until a turbidity appeared. The turbid solution was allowed to stand at room temperature when yellow crystals of tetraethylammonium bis(4-methyl-1,2-benzenedithiolato)methylgermanate(IV), $[(C_7H_6S_2)_2GeMe][Et_4N]$ (2), deposited; mp 123–124 °C (yield 1.25 g, 90.3%). ^1H NMR (CD_3Cl_3/Me_4Si) (ppm): 7.2 (m, 4 H, aromatic protons of toluenedithiolato groups); 6.6 (m, 2 H, aromatic protons of toluenedithiolato groups); 2.95 (q, 8 H, CH_2 protons of Et_4N^+); 2.15 (s, 6 H, CH_3 protons of toluenedithiolato groups); 1.55 (s, 3 H, $GeCH_3$); 1.05 (m, 12 H, CH_3 protons of Et_4N^+). Anal. Calcd for $C_{23}H_{35}S_4NGe$: C, 52.74; H, 6.76; N, 2.59. Found: C, 52.47; H, 6.7; N, 2.66.

Tetraethylammonium Bis(3,4,5,6-tetrachloro-1,2-benzenediolato)methylgermanate(IV), $[(C_6Cl_4O_2)_2GeMe][Et_4N]$ (3). To a solution of the 1:1 adduct of triphenylphosphine oxide and tetrachlorocatechol, $Ph_3P{=}O{\cdot}C_6Cl_4(OH)_2$ (2.3 g, 4.37 mmol), was added methylgermanium trichloride (0.424 g, 2.185 mmol). Triethylamine (0.883 g, 8.74 mmol) was added to this mixture under vigorous stirring when an exothermic reaction occurred and a white precipitate was thrown out of the solution. The resulting mixture was stirred at room temperature for $^1/_4$ h and then heated under reflux for 1 h. The reaction mixture was cooled to room temperature and filtered to remove the precipitate of triethylammonium hydrochloride. Evaporation of solvent from the filtrate gave a semisolid residue, which was extracted three times with hexane (20 mL) to dissolve the triphenylphosphine oxide byproduct in the reaction. The insoluble residue was dissolved in acetonitrile (30 mL), and to the solution was added tetraethylammonium chloride (0.36 g, 2.185 mmol). When the mixture was stirred, a light brown solution formed and a silky white precipitate of $Et_3NH^+Cl^-$ was thrown out of the solution. Removal of the solvent in vacuo afforded a brown solid, which was washed with water to remove triethylammonium chloride formed in the metathesis reaction. The insoluble solid was filtered off under suction, dried under oil-pump vacuum at room temperature, and dissolved in a minimum volume of boiling acetonitrile to obtain a brown solution. Cooling the solution to room temperature yielded colorless crystals of tetraethylammonium bis(3,4,5,6-tetrachloro-1,2-benzenediolato)methylgermanate(IV), $[(C_6Cl_4O_2)_2GeMe][Et_4N]$ (3), mp > 260 °C (yield 1.5 g, 96.7%). ^1H NMR (CD_3CN/Me_4Si, 10% solution) (ppm): 3.15 (q, 8 H, CH_2 protons of Et_4N^+); 1.2 (m, 12 H, CH_3 protons of Et_4N^+); 0.85 (s, 3 H, CH_3 protons of $GeCH_3$). Anal. Calcd for $C_{21}H_{23}O_4NCl_8Ge$: C, 35.54; H, 3.26; N, 1.97. Found: C, 36.08; H, 3.18; N, 1.96.

Tetraethylammonium Bis(4-methyl-1,2-benzenedithiolato)phenylgermanate, $[(C_7H_6S_2)_2GePh][Et_4N]$ (4). To a solution of toluene-3,4-dithiol (1.563 g, 10 mmol) and phenylgermanium trichloride (1.28 g, 5 mmol) in benzene (50 mL) was added under vigorous stirring triethylamine (2.02 g, 20 mmol). An immediate exothermic reaction occurred, and a flocculent white precipitate was thrown out of the solution. The resulting mixture was stirred at room temperature for 10 min and then heated under reflux for 1 h. Filtration of the reaction mixture at room temperature followed by evaporation of the solvent from the filtrate afforded a viscous residue embedded in a crystalline solid ($Et_3NH^+Cl^-$). The residue was dissolved in acetonitrile (20 mL), and to the solution was added tetraethylammonium chloride (0.825 g, 5 mmol). The mixture was stirred for 5 min at room temperature and then solvent evaporated to dryness. Water (50 mL) was added to the solid residue, and the mixture was magnetically stirred for 5 min to dissolve the triethylammonium chloride. The water-insoluble yellow viscous mass solidified when the suspension was chilled in an ice–water bath for $^1/_4$ h. Decantation of the aqueous solution afforded a yellow crystalline solid, which was dried under oil-pump vacuum at room temperature. The foamy solid thus obtained was dissolved in a minimum volume of acetone at room temperature, and to the yellow solution was added dropwise hexane until a turbidity appeared. The turbid solution was cooled in a refrigerator at 0 °C for 3 days when flesh-colored crystals deposited. The crude crystals were separated and recrystallized from a mixture of acetone and hexane at 0 °C to obtain pure tetraethylammonium bis(4-methyl-1,2-benzendithiolato)phenylgermanate(IV), $[(C_7H_6S_2)_2GePh][Et_4N]$ (4), mp 125–126 °C (yield 2.67 g, 90.7%). ^1H NMR (CD_3CN/Me_4Si) (ppm): 7.8 (m, 2 H, ortho protons of GePh); 7.17 (m, 7 H, meta and para protons of GePh and γ and δ protons of toluenedithiolate groups); 6.60 (m, 2 H, α protons of toluenedithiolato groups); 3.05 (q, 8 H, CH_2 protons of Et_4N^+); 2.12 (s, 6 H, CH_3 protons of toluenedithiolato groups); 1.1 (m, 12 H, CH_3 protons of Et_4N^+). Anal. Calcd for $C_{28}H_{37}S_4NGe$: C, 57.15; H, 6.34; N, 2.38. Found: C, 57.32; H, 6.61; N, 2.41.

Crystallography. Crystals were mounted inside sealed thin-walled glass capillaries as a precaution against moisture sensitivity. Data were collected by using the θ–2θ scan mode: $2° \leq 2\theta_{\mathrm{mo\,K\alpha}} \leq 50°$ for 1 and 3; $2° \leq 2\theta_{\mathrm{Mo\,K\alpha}} \leq 43°$ for 2. No corrections were made for absorption. The structures for 1 and 2 were solved by using Patterson and difference Fourier techniques, while 3 was solved by a combination of direct methods (MULTAN) and difference Fourier techniques. Refinement was done by using full-matrix least squares.[15]

X-ray Crystallographic Studies for $[(C_6H_4O_2)_2GeMe][Et_4N]$ (1). The colorless to pale gray-blue crystal used for the X-ray studies (0.30 × 0.35 × 0.40 mm) was cut from a polycrystalline mass.

Crystal Data for $C_{21}H_{31}O_4NGe$ (1): tetragonal space group $P4_12_12$ (D_4^4-No. 92),[16] $a = b = 9.834$ (4) Å, $c = 22.275$ (7) Å, $Z = 4$, $\mu_{\mathrm{Mo\,K\alpha}} = 1.532\ \mathrm{mm}^{-1}$. A total of 1172 independent reflections ($+h,+k,+l$ for $|h| \geq |k|$) were measured. The 15 independent non-hydrogen atoms were refined anisotropically. The 8 independent aromatic and methylene hydrogen atoms were included in the refinement as fixed isotropic scatterers whose coordinates were updated as refinement converged so that the final C–H bond lengths were 0.98 Å. Methyl hydrogen atoms were omitted from the refinement. The final agreement factors[17,18] were $R = 0.045$ and $R_w = 0.064$ for the 989 reflections having $I \geq 2\sigma_I$.

X-ray Crystallographic Studies for $[(MeC_6H_3S_2)_2GeMe][Et_4N]$ (2). 2 grows as bright yellow clusters of small spearlike crystals, which diffract poorly. The crystal used for the X-ray studies had dimensions of 0.10 × 0.15 × 0.25 mm.

Crystal Data for $C_{23}H_{35}S_4NGe$ (2): orthorhombic space group $Pbca$ (D_{2h}^{15}-No. 61),[19] $a = 15.344$ (2) Å, $b = 19.920$ (5) Å, $c = 17.017$ (5) Å, $Z = 8$, $\mu_{\mathrm{Mo\,K\alpha}} = 1.565\ \mathrm{mm}^{-1}$. A total of 2971 independent reflections ($+h,+k,+l$) were measured. Of the 29 independent non-hydrogen atoms, 28 were refined anisotropically in full occupancy, while the 29th independent non-hydrogen atom, which is disordered, having two possible positions, was refined as two anisotropic atoms having half-occupancy. The 13 independent aromatic and methylene hydrogen atoms were included in the refinement in the same manner as described for 1. Methyl hydrogen atoms were omitted from the refinement. The final agreement factors[17] were $R = 0.065$ and $R_w = 0.070$ for the 1477 reflections having $I \geq 2\sigma_I$.

X-ray Crystallographic Studies for $[(C_6Cl_4O_2)_2GeMe][Et_4N]$ (3). The crystal used for data collection (0.25 × 0.30 × 0.35 mm) was cut from a colorless rodlike crystal.

Crystal Data for $C_{21}H_{23}O_4NCl_8Ge$ (3): monoclinic space group $P2_1/c$ (C_{2h}^5-No. 14),[20] $a = 10.011$ (2) Å, $b = 16.793$ (3) Å, $c = 16.386$ (5) Å, $\beta = 93.78$ (2)°, $Z = 4$, $\mu_{\mathrm{Mo\,K\alpha}} = 1.982\ \mathrm{mm}^{-1}$. A total of 4820 independent reflections ($+h,+k,\pm l$) were measured. The 35 independent non-hydrogen atoms were refined anisotropically. The 3 independent methyl hydrogen atoms of the anion were located on a difference Fourier synthesis and were included in the refinement as fixed isotropic scatterers. The 8 independent methylene hydrogen atoms were treated as described for 1. The methyl hydrogen atoms of the cation were omitted from the refinement. The final agreement factors[17] were $R = 0.049$ and $R_w = 0.072$ for the 3704 reflections having $I \geq 2\sigma_I$.

Results

The atom-labeling scheme for 1 is shown in the ORTEP plot of Figure 1. Atomic coordinates are given in Table I while selected

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(15) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{1/2} = 2F_oLp/\sigma_I$. Mean atomic scattering factors were taken from ref 16 (1974; Vol. IV, pp 72–98). Real and imaginary dispersion corrections for Ge, S, and O were taken from the same source (pp 149–150).

(16) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. I, p 182.

(17) $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$.

(18) Refinement in $P4_32_12$ gave $R = 0.051$ and $R_w = 0.072$.

(19) Reference 16, p 150.

(20) Reference 16, p 99.

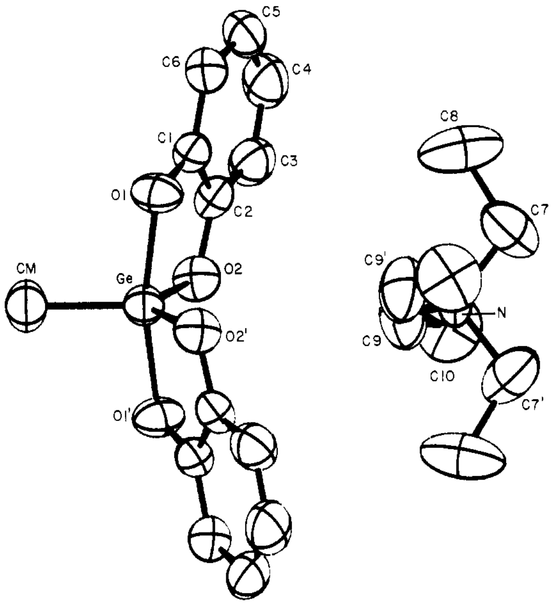


Figure 1. ORTEP plot of $[(C_6H_4O_2)_2GeMe][Et_4N]$ (**1**) with thermal ellipsoids at the 50% probability level. Primed atoms are related to unprimed ones by *y*, *x*, −*z*. Hydrogen atoms are omitted for purposes of clarity.

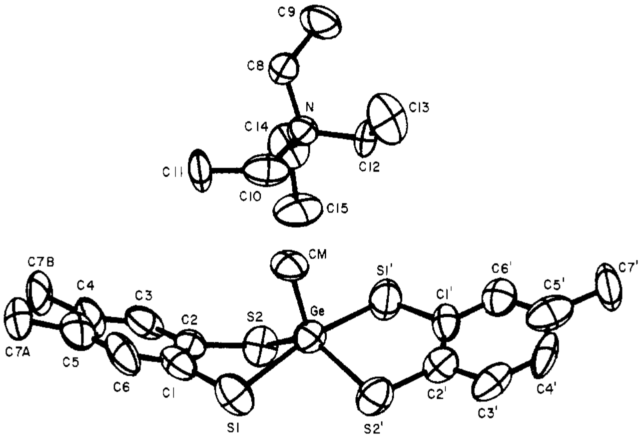


Figure 2. ORTEP plot of $[(MeC_6H_3S_2)_2GeMe][Et_4N]$ (**2**) with thermal ellipsoids at the 50% probability level. Both positions for the disordered methyl group (C7A and C7B) are shown. Hydrogen atoms are omitted for purposes of clarity. Primed atoms are *not* related crystallographically to unprimed ones.

Table I. Atomic Coordinates in Crystalline $[(C_6H_4O_2)_2GeMe][NEt_4]$ (**1**)[a]

atom type[b]	10^4x	10^4y	10^4z
Ge	137 (1)	137 (1)	0[c]
N	3836 (5)	3836 (5)	0[c]
CM	−1262 (8)	−1262 (8)	0[c]
O1	−325 (5)	929 (5)	761 (2)
O2	−269 (6)	1801 (5)	−326 (2)
C1	−763 (7)	2208 (8)	678 (3)
C2	−745 (7)	2696 (8)	94 (3)
C3	−1141 (9)	3994 (9)	−35 (5)
C4	−1628 (10)	4817 (10)	402 (5)
C5	−1668 (10)	4368 (10)	990 (5)
C6	−1226 (9)	3023 (10)	1133 (4)
C7	3799 (12)	5189 (11)	332 (5)
C8	2427 (14)	5405 (16)	686 (5)
C9	2686 (12)	3746 (12)	−433 (5)
C10	2610 (13)	4926 (13)	−906 (5)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 1. [c] Fixed.

bond lengths and angles are given in Table II. The corresponding information for **2** is given in Figure 2 and in Tables III and IV, while the corresponding information for **3** is given in Figure 3 and in Tables V and VI. Hydrogen atom parameters, additional bond lengths and angles, thermal parameters, and deviations from selected least-squares mean planes are provided as supplementary material.

Table II. Selected Bond Lengths (Å) and Bond Angles (deg) for $[(C_6H_4O_2)_2GeMe][Et_4N]$ (**1**)[a,b]

Ge–CM	1.946 (6)	O1–C1	1.343 (9)
Ge–O1	1.920 (5)	O2–C2	1.367 (9)
Ge–O2	1.834 (5)		
O1–Ge–O1′	166.3 (3)	O2–Ge–O1	86.3 (2)
O2–Ge–O2′	123.1 (4)	Ge–O1–C1	109.6 (4)
CM–Ge–O2	118.5 (2)	Ge–O2–C2	112.2 (4)
CM–Ge–O1	96.8 (2)	O1–C1–C2	116.7 (7)
O2′–Ge–O1	87.2 (2)	O2–C2–C1	115.0 (7)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 1.

Table III. Atomic Coordinates in Crystalline $[(MeC_6H_3S_2)_2GeMe][Et_4N]$ (**2**)[a]

atom type[b]	10^4x	10^4y	10^4z
Ge	1641 (1)	1379 (1)	1615 (1)
S1	1820 (2)	182 (2)	1754 (2)
S1′	1200 (3)	2477 (2)	1226 (2)
S2	189 (2)	1189 (2)	1785 (2)
S2′	2474 (3)	1323 (2)	515 (2)
CM	2245 (9)	1604 (6)	2602 (7)
C1	998 (9)	100 (6)	2487 (9)
C2	270 (9)	521 (6)	2469 (7)
C3	−379 (9)	424 (7)	3031 (9)
C4	−349 (11)	−48 (7)	3591 (9)
C5	379 (12)	−442 (8)	3667 (9)
C6	1059 (10)	−361 (6)	3106 (9)
C7A	364 (16)	−894 (13)	4342 (14)
C7B	−890 (19)	−200 (14)	4241 (17)
C1′	2054 (8)	2659 (6)	543 (7)
C2′	2559 (9)	2162 (7)	228 (7)
C3′	3165 (9)	2361 (8)	−341 (7)
C4′	3224 (10)	3050 (8)	−560 (7)
C5′	2702 (10)	3548 (9)	−247 (8)
C6′	2127 (9)	3340 (7)	308 (8)
C7′	2814 (11)	4275 (7)	−516 (9)
N	197 (6)	3265 (4)	3580 (5)
C8	359 (8)	3539 (6)	4406 (7)
C9	156 (10)	4294 (6)	4504 (8)
C10	548 (8)	2533 (8)	3563 (8)
C11	97 (9)	2020 (6)	4114 (8)
C12	664 (9)	3678 (6)	2973 (7)
C13	1652 (9)	3805 (7)	3101 (10)
C14	−777 (8)	3243 (7)	3420 (9)
C15	−1031 (9)	2888 (8)	2655 (8)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 2.

Table IV. Selected Bong Lengths (Å) and Bond Angles (deg) for $[(MeC_6H_3S_2)_2GeMe][Et_4N]$ (**2**)[a,b]

Ge–S1	2.413 (4)	S1–C1	1.78 (1)
Ge–S1′	2.383 (4)	S1′–C1′	1.79 (1)
Ge–S2	2.278 (4)	S2–C2	1.77 (1)
Ge–S2′	2.269 (4)	S2′–C2′	1.75 (1)
Ge–CM	1.97 (1)		
S1–Ge–S1′	165.2 (2)	Ge–S1–C1	94.5 (4)
S2–Ge–S2′	130.4 (2)	Ge–S1′–C1′	99.1 (5)
CM–Ge–S1	95.0 (4)	Ge–S2–C2	98.0 (5)
CM–Ge–S1′	99.3 (4)	Ge–S2′–C2′	103.0 (5)
CM–Ge–S2	112.9 (4)	S1–C1–C2	120 (1)
CM–Ge–S2′	116.7 (4)	S1′–C1′–C2′	122 (1)
S1–Ge–S2	86.3 (1)	S2–C2–C1	121 (1)
S1′–Ge–S2′	88.7 (1)	S2′–C2′–C1′	123 (1)
S1–Ge–S2′	88.1 (1)		
S1′–Ge–S2	84.9 (1)		

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 2.

Table V. Atomic Coordinates in Crystalline $[(C_6Cl_4O_2)_2GeMe][Et_4N]$ (**3**)[a]

atom type[b]	10^4x	10^4y	10^4z
Ge	4736.2 (6)	3732.4 (3)	2355.9 (3)
Cl3	7638 (1)	3908 (1)	85 (1)
Cl4	5931 (2)	4225 (1)	−1566 (1)
Cl5	2831 (2)	4168 (1)	−1599 (1)
Cl6	1411 (2)	3952 (1)	50 (1)
Cl3′	7994 (2)	5495 (1)	3749 (1)
Cl4′	6556 (2)	6736 (1)	4854 (1)
Cl5′	3473 (2)	6643 (1)	4973 (1)
Cl6′	1810 (2)	5312 (1)	4012 (1)
O1	3385 (4)	3777 (2)	1509 (2)
O2	5928 (4)	3724 (3)	1513 (2)
O1′	6057 (4)	4348 (2)	2917 (2)
O2′	3526 (4)	4294 (2)	2982 (2)
C1	3880 (5)	3844 (3)	772 (3)
C2	5288 (5)	3821 (3)	784 (3)
C3	5900 (5)	3917 (3)	58 (3)
C4	5165 (6)	4033 (3)	−674 (3)
C5	3766 (6)	4032 (3)	−680 (3)
C6	3142 (5)	3944 (3)	47 (4)
C1′	4136 (6)	4851 (3)	3455 (3)
C2′	5542 (5)	4888 (3)	3409 (3)
C3′	6272 (6)	5452 (3)	3844 (3)
C4′	5641 (6)	6000 (4)	4338 (4)
C5′	4267 (7)	5957 (4)	4380 (4)
C6′	3539 (6)	5383 (4)	3942 (3)
C7	4786 (6)	2682 (4)	2789 (4)
N	9778 (4)	2929 (3)	2636 (3)
C8	9048 (7)	3665 (5)	2313 (4)
C9	9951 (9)	4370 (4)	2105 (5)
C10	8737 (6)	2292 (5)	2768 (4)
C11	9325 (8)	1475 (5)	3052 (6)
C12	10617 (7)	3119 (5)	3416 (4)
C13	9808 (9)	3408 (6)	4130 (4)
C14	10762 (6)	2632 (4)	2030 (4)
C15	10082 (8)	2361 (4)	1208 (4)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 3.

Table VI. Selected Bond Lengths (Å) and Bond Angles (deg) for $[(Cl_4C_6O_2)_2GeMe][Et_4N]$ (**3**)[a,b]

Ge–O1	1.874 (4)	O1–C1	1.340 (6)
Ge–O2	1.884 (4)	O2–C2	1.328 (6)
Ge–O1′	1.872 (4)	O1′–C2′	1.339 (6)
Ge–O2′	1.890 (4)	O2′–C1′	1.337 (6)
Ge–C7	1.901 (6)		
O1–Ge–O1′	142.5 (2)	Ge–O1–C1	112.3 (3)
O1–Ge–O2	85.3 (2)	Ge–O2–C2	111.6 (3)
O1–Ge–O2′	85.7 (2)	Ge–O1′–C2′	112.5 (3)
O1–Ge–C7	108.3 (2)	Ge–O2′–C1′	112.3 (3)
O1′–Ge–O2	84.4 (2)	O1–C1–C2	114.5 (5)
O1′–Ge–O2′	85.1 (2)	O2–C2–C1	116.0 (5)
O1′–Ge–C7	109.2 (2)	O2′–C1′–C2′	114.6 (5)
O2–Ge–O2′	149.4 (2)	O1′–C2′–C1′	115.2 (5)
O2–Ge–C7	105.3 (3)		
O2′–Ge–C7	105.2 (2)		

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 3.

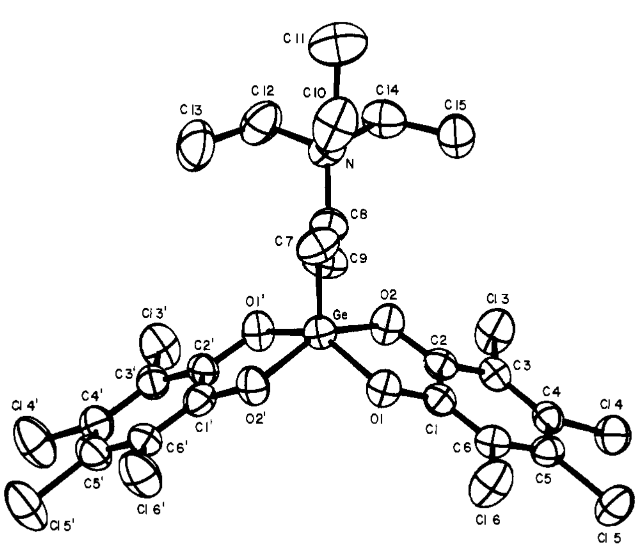
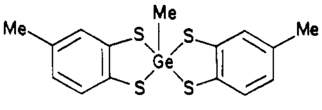


Figure 3. ORTEP plot of $[(C_6Cl_4O_2)_2GeMe][Et_4N]$ (**3**) with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for purposes of clarity. Primed atoms are *not* related crystallographically to unprimed ones.

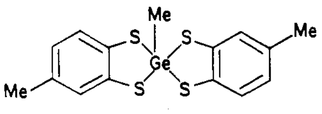
Discussion

Basic Structures. Both the cation and the anion in **1** have crystallographic 2-fold symmetry, with N, Ge, and CM lying on a 2-fold axis. The methyl hydrogen atoms of the anion are disordered about this 2-fold axis and were not apparent on difference Fourier syntheses.

The anion in **2** is apparently a 50:50 mixture of cis and trans isomers[21] that pack randomly with respect to the position of the disordered methyl group.



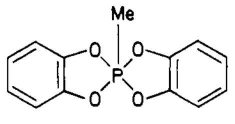
cis



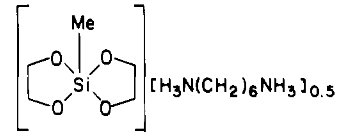
trans

The geometry about the Ge atom for each of the three compounds lies on the coordinate connecting a trigonal bipyramid to a rectangular pyramid having four basal chalcogen atoms and an apical methyl group, where the methyl carbon atom is pivotal in the Berry pseudorotation process.[22,23] By the dihedral angle method to access displacement,[7,24,25] **1** is displaced 21.3% (22.6% by using unit vectors) from the TBP toward the RP. The corresponding values for **2** and **3** are 41.3% (37.1%) and 85.0% (85.5%), respectively.

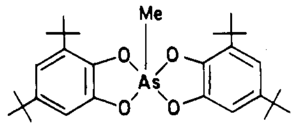
The structural displacement from the trigonal bipyramid for the methylgermanate **1** appears relatively small when compared with the displacements for the five-coordinated derivatives **5**[26] and **6**.[27] However, the displacement of **1** is similar to that found for the arsorane **7**.[28] The inductive effect of the *tert*-butyl groups



5, **79%**



6, **53.3%**



7, **22.5%**

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(21) The occupancy of the half-atoms was not refined. The assignment of 50% occupancy was based on the near equivalence of the electron density for the two positions on a difference Fourier synthesis and on the near equivalence of the refined thermal parameters when both sites were assigned half-occupancy.

(22) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.

(23) Reference 13, Chapter 3.

(24) Reference 13, p 34 ff.

(25) Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748.

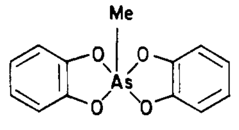
(26) Wunderlich, H. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1974**, *B30*, 939.

(27) Schomburg, D. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 195.

(28) Poutasse, C. A.; Day, R. O.; Holmes, J. M.; Holmes, R. R. *Organometallics* **1985**, *4*, 708.

in enhancing As–O bond pair repulsions was cited[28] as an explanation favoring the appearance of the TBP for **7**.

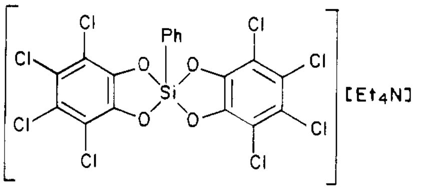
A similarly structured anionic silicate, [$(t\text{-}Bu_2C_6H_2O_2)_2SiPh$][$Et_3NH$] (**8**) (29.0%),[29] favors the trigonal-bipyramid geometry comparably to the arsorane **7**. Since the arsorane **9**[30] has a structure more like the analogous phosphorane **5**,[26] both of which lack ionic lattice effects, it appears then that the low structural distortion of **1** from the trigonal bipyramid is associated with this lattice effect. As the central atom becomes more metallic, going down the periodic table, ionic lattice effects are expected to assume increasing importance.



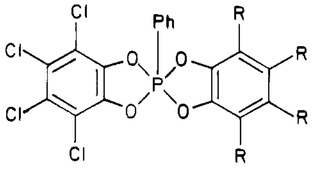
9, 72.2%

The replacement of oxygen atoms by sulfur atoms on going from **1** to **2** gives an expected shift in structure favoring the rectangular pyramid. Insertion of the larger less electronegative sulfur atoms should lessen the charge effect associated with the ionic lattice as felt at germanium.

The structure of the chloro-substituted germanate **3**, near the rectangular pyramid, follows the trend for electron-withdrawing ring atoms. The electron withdrawal reduces bond electron pair effects at the central atom and allows the normally higher energy rectangular pyramid to become stabilized. The structures of the related anionic silicate **10**[31] and phosphoranes **11** and **12**[32] are very close to that of the anionic germanate **3**.



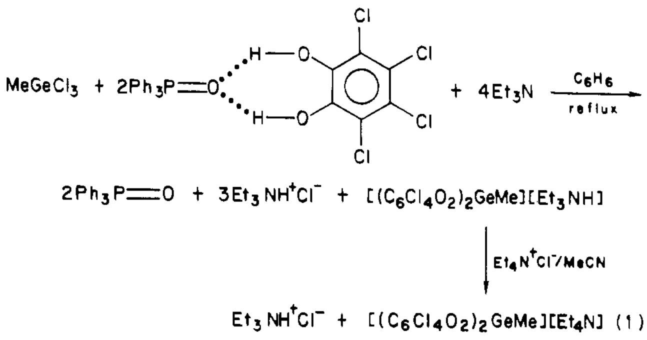
10, 89.8%



11, R = H, 94%
12, R = Cl, 94%

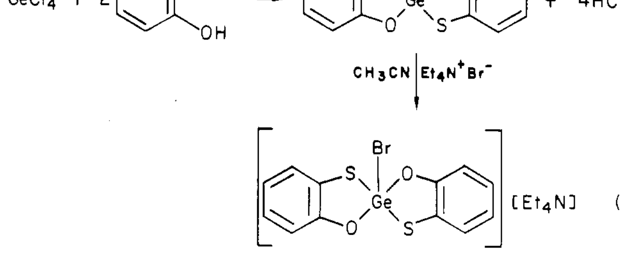
Synthetic Aspects. All of the anionic germanates, **1–4**, were prepared by the benzene solution reaction of an organogermanium trichloride with a catechol or a thiocatechol derivative in the presence of Et_3N. The resultant Et_3NH^+ complexes were metathetically exchanged in acetonitrile to form the Et_4N^+ salts. This reaction sequence is illustrated for the formation of **3** in eq 1.

In view of the commercial nonavailability of tetrachlorocatechol and its preparation involving a tedious procedure of chlorination of catechol,[33] the 1:1 adduct of triphenylphosphine oxide and tetrachlorocatechol, $Ph_3P{=}O{\cdot}C_6Cl_4(OH)_2$, was used as an alternative source to carry out the preparation of **3**. The 1:1 adduct was prepared by the reaction of $Ph_3P{=}O$ with *o*-chloranil in moist ether. The triphenylphosphine oxide byproduct resulting in the reaction sequence (1) could be easily separated from the desired reaction product by a selective extraction with benzene.



(1)

The synthetic route to obtain the pentacoordinated methylgermanates, **1–4**, contrasts with syntheses for related anionic halogermanates containing catechol,[5] toluene-3,4-dithiol,[5] or *o*-mercaptophenol[2] as the cyclic components. In these cases the tetracoordinated spirocyclic system is first formed. Reaction of the latter with the appropriate halide reagent yields the desired product. This sequence is illustrated in forming the mixed-ligand species [$(C_6H_4OS)_2GeBr$][Et_4N][2] (eq 2). The formations of pentacoordinated spirocyclic anionic halosilicates[34] and halostannates,[14,35] in general, follow analogous preparative routes, i.e., eq 2. For five-coordinated silicates containing an aryl or alkyl group as the fifth ligand, a trialkoxyorganosilane is the choice of the silicon-containing reagent.[1,31,36] Little is known about related five-coordinated anionic stannates similarly substituted with an aryl or alkyl group.



(2)

Distortion Coordinate. With the inclusion of the previous halo and hydroxy germanates **13–19**,[2-4] the methyl derivatives **1–3** reported here, and the related phenyl analogues **20–22**,[11] a sufficient number of pentacoordinated anionic germanates have been structurally characterized to provide a meaningful description of their solid-state distortions.

A convenient measure of structural distortion for pentacoordinated molecules[7,24,25] is obtained by plotting the values of the trans basal angles θ_{15} and θ_{24} of the RP (which are axial and equatorial angles with reference to the TBP) vs. the dihedral angle δ_{24}.[37]

Figure 4 displays a θ vs. δ_{24} graph for the 13 germanates that have been structurally characterized by X-ray analysis. These data are summarized in Table VII. The lines shown are determined by the θ values of 120 and 180° for the ideal trigonal bipyramid, which has $\delta_{24} = 53.1°$, and the θ value of 150.1° for the "limiting" rectangular pyramid. The latter value is obtained from a least-squares fit to the data. The least-squares lines are given in the caption for Figure 4. It is seen that the Berry coordinate is well followed for five-coordinated germanates. A comparison of this type of plot for phosphoranes,[7,8,24] arsoranes,[10]

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(29) Holmes, R. R.; Day, R. O.; Chandrasekhar, V.; Holmes, J. M. *Inorg. Chem.* **1985**, *24*, 2009.

(30) Wunderlich, H. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 1000.

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(32) Clark, T. E.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1979**, *18*, 1668.

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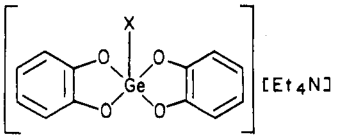
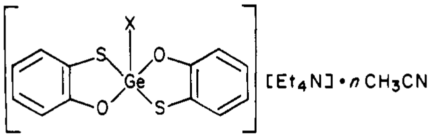
(36) Holmes, R. R.; Day, R. O.; Harland, J. J.; Holmes, J. M. *Organometallics* **1984**, *3*, 347.

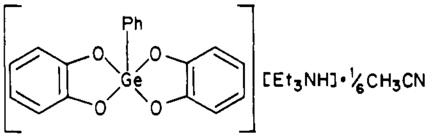
(37) The latter angle is the dihedral angle formed between normals to the TBP faces 124 and 245 that have the common equatorial edge 24 (see Table VII) and is the one most intimately associated with the Berry exchange coordinate.[22] This dihedral angle has a value of 53.1° for an idealized TBP but becomes 0° as edge 24 disappears on forming the RP.



13, X = F
14, X = Cl
15, X = Br
20, X = Ph



16, X = Cl, n = 0
17, X = Br, n = 1



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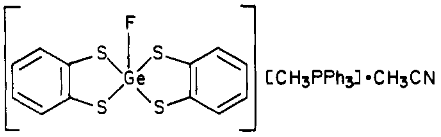

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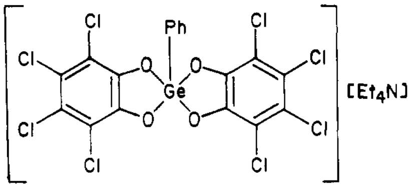
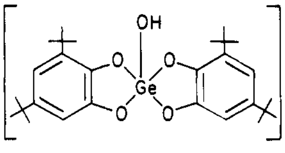


22



19

and five-coordinated silicon compounds[31] indicates a similar scatter of points as well as a "limiting" rectangular pyramid with a trans basal θ angle near 150°.

A more elaborate means of expressing geometrical distortion is to use the sum of dihedral angle method, which has been adequately described.[7] Comparison of the dihedral angle sum for a compound of interest, $\sum_i|\sigma_i(\mathrm{C}) - \sigma_i(\mathrm{TBP})|$, with a similar sum, $R = \sum_i|\sigma_i(\mathrm{TBP}) - \sigma_i(\mathrm{RP})|$ (which is equal to 217.7° when $\theta = 150°$), for the two "idealized" geometries for pentacoordinated derivatives allows the calculations of a percent displacement between these two geometries from the TBP to the RP. A dihedral-angle plot obtained from application of this method on a common reference scale[7] is given in Figure 5 for the germanates listed in Table VII. Again, the Berry coordinate is seen to be followed closely.

As the structures become more rectangular pyramidal, the axial and equatorial ring Ge–O bond lengths converge (Table VII). This is shown graphically in Figure 6, where the axial–equatorial bond difference, Δ, is expressed as a function of the dihedral angle, δ_{24}. Since hydrogen bonding causes a lengthening of the affected Ge–O bonds,[36] these bonds are not included in obtaining Δ values.

By separate treatment of the axial and equatorial ring Ge–O bond length data, a range of 0.06 Å is obtained for Ge–O equatorial bond lengths and a value of 1.848 Å is indicated for the "limiting" RP. The least-squares equation is Ge–O$_{\mathrm{eq}}$ = $-0.000202\delta_{24} + 1.845$. A comparison with phosphoranes,[7] the

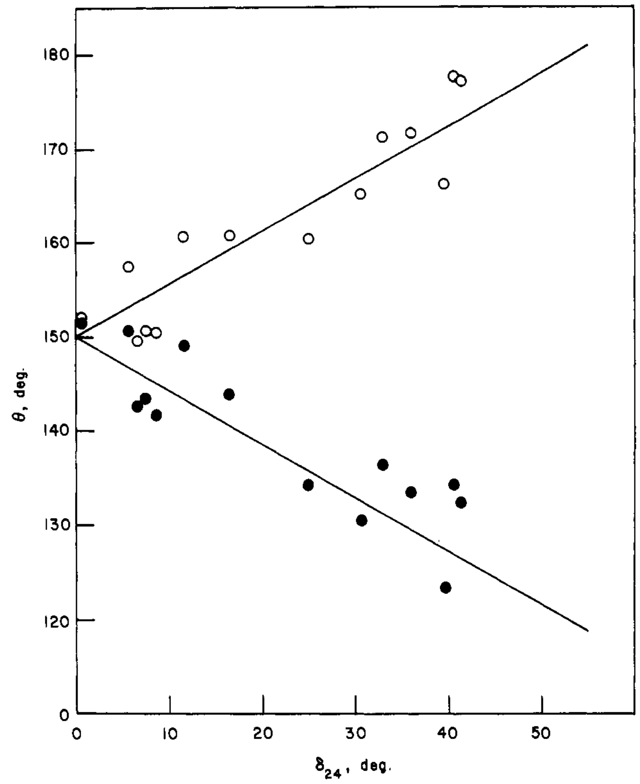


Figure 4. Variations of the axial angle θ_{15} (open circles) and equatorial angle θ_{24} (filled circles) vs. the dihedral angle δ_{24} as structural distortion for pentacoordinated germanium(IV) compounds listed in Table VII proceeds along the Berry coordinate from a rectangular pyramid toward a trigonal bipyramid. The least-squares lines, $\theta_{15} = 0.5548\delta_{24} + 149.7$ and $\theta_{24} = -0.5346\delta_{24} + 150.4$, give a value of 150.1° for the θ angle of the "limiting" rectangular pyramid.

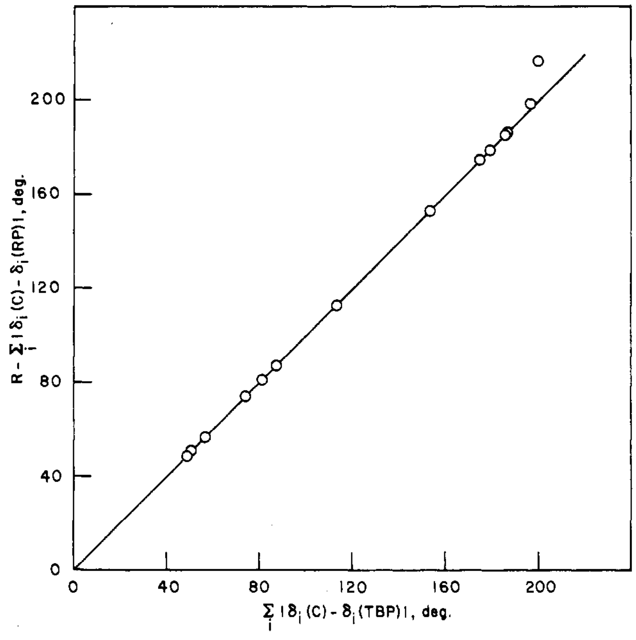
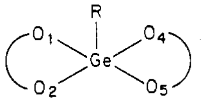


Figure 5. Sum of the dihedral angles for pentacoordinated germanium(IV) compounds listed in Table VII from a rectangular-pyramidal geometry vs. the sum from a trigonal bipyramid on a common reference scale.

isoelectronic five-coordinated anionic silicates,[36] and arsoranes[10] shows 0.04, 0.05, and 0.06 Å ranges, respectively, for equatorial ring M–O bond lengths. The axial Ge–O bond lengths in Table VII exhibit too much scatter to obtain a meaningful comparison.

The ease with which these pentacoordinated spirocyclic germanium(IV) compounds undergo geometrical changes suggests that they belong to a class of nonrigid molecules similar to that

Table VII. Axial and Equatorial Angles (θ) (deg), Dihedral Angles (δ) (deg), and Ge–O Bond Lengths (Å) for Pentacoordinated Anionic Germanates



compd no.	δ_{24}	θ_{15}	θ_{24}	$\mathrm{Ge{-}O_{ax}}$[a]	$\mathrm{Ge{-}O_{eq}}$[a]	Δ(ax–eq)	%(TPB → RP)[b]	ref[c]
1[d]	39.6	166.3	123.1	1.920 (1) (5)	1.834 (2) (4)	0.086	22.6	this work
17A[e]	40.3	174.6	131.1	1.906 (1)			26.2	2
				1.906 (5)				
17B	41.4	174.5	129.7	1.905 (1)			23.6	2
				1.904 (5)				
16	36.0	171.9	133.5	1.898 (1)			34.2	2
				1.899 (5)				
2	33.0	165.2	130.4				37.1	this work
18	33.0	171.1	136.2				40.3	4
20	25.0	160.3	134.1	1.903 (1)	1.859 (2)	0.044	51.8	11
				1.892 (5)	1.851 (4)	0.041		
15	16.5	160.8	143.9	1.851 (1)	1.832 (2)	0.019	70.4	2
				1.834 (5)	1.813 (4)	0.021		
13	11.6	160.8	149.0	1.839 (1)	1.831 (2)	0.008	80.6	4
				1.835 (5)	1.825 (4)	0.010		
21	8.7	150.5	141.8	1.874 (1)[f]	1.832 (2)		82.2	11
				1.858 (5)	1.870 (4)[f]			
22	7.3	150.7	143.3	1.879 (1)	1.859 (2)	0.020	85.2	11
				1.870 (5)	1.884 (4)	−0.014		
3	6.9	149.4	142.5	1.884 (1)	1.874 (2)	0.010	85.5	this work
				1.890 (5)	1.872 (4)	0.018		
14	5.9	157.5	151.6	1.852 (1)	1.824 (2)	0.028	90.7	3
				1.842 (5)	1.811 (4)	0.031		
19	0.7	152.0	151.3	1.839 (1)	1.853 (2)	−0.014	95.7	2
				1.866 (5)	1.825 (4)	0.041		

[a] The numbers in parentheses are atom identifications relative to the figure given below the table heading. [b] Based on unit bond distances. [c] These are references to the X-ray studies. [d] Compound **1** cotains a crystallographic 2-fold axis about germanium. [e] There are two independent molecules per unit cell for **17**. [f] Hydrogen-bonded Ge–O bonds. Since hydrogen bonding results in a lengthening of the affected Ge–O bonds, these bonds are not included in the calculation of Δ.

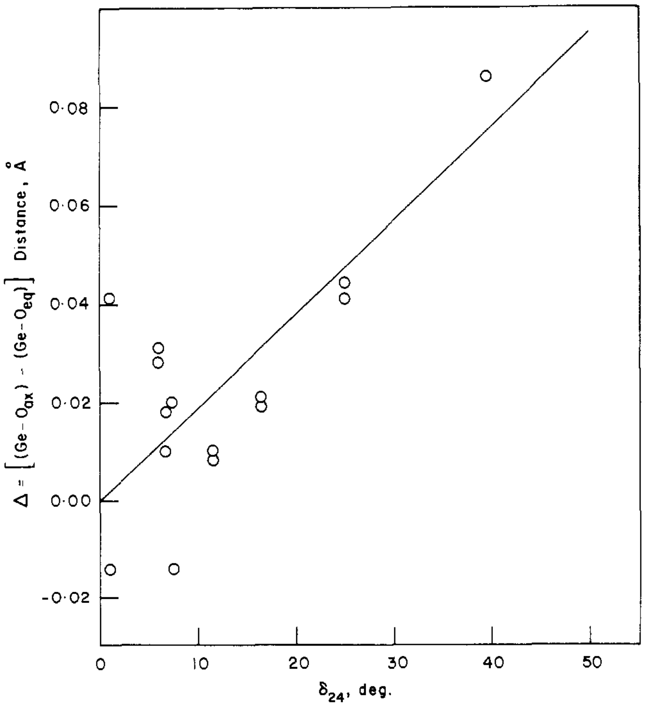


Figure 6. Differences in axial and equatorial ring Ge–O bond lengths (Δ) for the non-hydrogen-bonded Ge–O bonds vs. the dihedral angle δ_{24}. The numbers refer to compound entries in Table VII. The least-squares line is $\Delta = 0.001882\delta_{24} + 0.000489$.

encountered with phosphoranes.[8,23] For the most part, the structural variations are understandable in terms of substituent effects[2,4,11] and follow the same trends cited in the introduction for phosphoranes.[6,12] The "limiting" rectangular pyramid, like that for five-coordinated phosphorus,[8,24] arsenic,[10] and silicon,[31] has a trans basal angle close to 150°. This contrasts with the geometry of five-coordinated transition-metal complexes where θ values for the rectangular pyramid are found to vary in the range of 140–175° depending on d orbital configuration.[38,39]

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Registry No. **1**, 99828-92-9; *cis*-**2**, 99828-94-1; *trans*-**2**, 99883-26-8; **3**, 99828-96-3; **4**, 99828-98-5; $\mathrm{MeGeCl_3}$, 993-10-2; $\mathrm{Ph_3P{=}O{\cdot}C_6Cl_4(OH)_2}$, 22400-36-8; $\mathrm{PhGeCl_3}$, 1074-29-9; catechol, 120-80-9; toluene-3,4-dithiol, 496-74-2.

Supplementary Material Available: Table A, thermal parameters for **1**; Table B, thermal parameters for **2**; Table C, thermal parameters for **3**; Table D, hydrogen atom parameters for **1**; Table E, hydrogen atom parameters for **2**; Table F, hydrogen atom parameters for **3**; Table G, additional bond lengths and angles for **1**; Table H, additional bond lengths and angles for **2**; Table I, additional bond lengths and angles for **3**; Table J, deviations from selected least-squares mean planes for **1**; Table K, deviations from selected least-squares mean planes for **2**; Table L, deviations from selected least-squares mean planes for **3**; and a listing of observed and calculated structure factor amplitudes for **1**–**3** (36 pages). Ordering information is given on any current masthead page.

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(38) Holmes, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 3745.
(39) Holmes, R. R. *Prog. Inorg. Chem.* **1984**, *32*, 119–235.
(40) The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)