density peaks imply that each TMPD molecule used as an attempted template had been fissioned into three triatomic species during incorporation into the $AlPO_4$-21 structure. These species probably consist of two dimethylammonium and one propyl species. For each unit cell, the $Al_{12}P_{12}O_{48}(OH)_4$ framework lacks four positive charges, which could be balanced by some combination of the four dimethylammonium and propyl species; both charged and uncharged species are needed. Nuclear magnetic resonance spectroscopy should provide an accurate identification. Although the occluded species fit neatly into the channels, the occurrence of two orientations of the triatomic species suggests that any templating control is weak at best. The doubling of high-angle diffractions might result from small changes of cell dimension induced by the different orientations; if so, each single crystal is actually an aggregate of two types of crystallites in near-parallel orientation. Electron micrography and energy loss spectroscopy might provide a test of this idea.

The subunits of the framework of $AlPO_4$-21 can be arranged in many different ways, and systematic enumeration is in progress. The twinning of $AlPO_4$-21 crystals is explained by a simple stacking fault.

Acknowledgment. The contribution by G.A., J.J.P., and J.V.S. was supported primarily by National Science Foundation Grant CHE 80-24138 and secondarily by the Materials Research Laboratory funded by NSF Grant 79-24007. We thank N. Weber for technical help and E. M. Flanigen, S. T. Wilson, and L. Patton for assistance and discussion.

Supplementary Material Available: Listings of observed and calculated structure factors (Table IV) and anisotropic displacement factors (Table V) (13 pages). Ordering information is given on any current masthead page.

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Stereochemically Nonrigid Five-Coordinated Germanates. Synthesis and Structure of Hydroxy- and Halo-Containing Spirocyclic Germanium(IV) Complexes[1,2]

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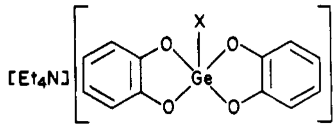
A series of five-coordinated anionic germanates containing oxygen and sulfur ligands, $[Et_4N][(C_6H_4OS)_2GeX]$ (X = F, Cl, Br, I), were synthesized from the newly formed spirocyclic compound $(C_6H_4OS)_2Ge$ and Et_4NX. Also formed was the hydroxy derivative $[Et_3NH][(C_6H_4OS)_2GeOH]$. The X-ray structures of chloro and bromo derivatives, **4** and **5**, respectively, were obtained as well as the structures of the previously prepared bromo and hydroxy catecholates, $[Et_4N][(C_6H_4O_2)_2GeBr]$ (**6**) and $[Et_3NH][(dtbc)_2GeOH]$ (**7**) (dtbc is 3,5-di-*tert*-butylcatechol). These compounds form a series, showing distortions from the trigonal bipyramid to the rectangular pyramid: **4** (34.2%); **5** (23.6, 26.2%); **6** (70.4%); **7** (95.7%). As with phosphoranes, the dominant criterion to stabilize the square or rectangular pyramid for pentacoordinate germanium is the presence of two unsaturated five-membered rings with like atoms in any one ring directly attached to the central atom. Comparisons with related silicon and tin anionic five-coordinated complexes suggest that stereochemical nonrigidity increases from silicon to germanium to tin. **4** crystallizes in the monoclinic space group *Cc* with a = 10.869 (3) Å, b = 12.852 (4) Å, c = 16.798 (4) Å, β = 103.00 (2)°, and Z = 4. **5** crystallizes in the monoclinic space group $P2_1$ with a = 12.345 (2) Å, b = 27.800 (5) Å, c = 7.779 (1) Å, β = 104.54 (1)°, and Z = 4. **6** crystallizes in the monoclinic space group $P2_1/c$ with a = 11.144 (1) Å, b = 10.916 (2) Å, c = 18.293 (2) Å, β = 96.89 (1)°, and Z = 4. **7** crystallizes in the orthorhombic space group $Pna2_1$ with a = 21.415 (5) Å, b = 16.279 (5) Å, c = 10.297 (3) Å, and Z = 4. The final conventional unweighted residuals were 0.037 (**4**), 0.051 (**5**), 0.059 (**6**), and 0.061 (**7**).

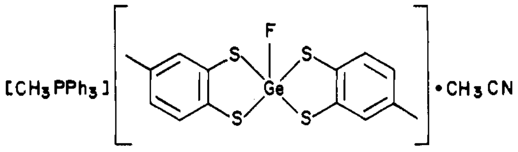
Introduction

Recent work[4,5] on five-coordinated compounds of main-group 4 elements has concentrated on anionic derivatives of silicon(IV) containing a spirocyclic framework. From the X-ray structural investigations, a distortion coordinate resulted[4] that was closely analogous to the Berry coordinate that was found earlier for phosphoranes.[6,7] This work resulted in the formulation of structural principles for five-coordinated silicon[5] that were comparable to those that apply to isoelectronic pentacoordinated phosphorus compounds.[6-9]

In an extension to related germanium complexes, the only examples that have been structurally characterized are the bis(benzenediolato)chlorogermanates[10] and -fluorogermanates,[11] **1** and **2**, respectively, and the corresponding bis(dithiolato)fluorogermanate[11] (**3**).



1, X = Cl
2, X = F



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In the interest of providing a wider range of five-coordinated anionic germanates, we have synthesized the halo derivatives, **4** and **5**, containing mixed ligands attached to germanium and have determined their molecular structures along with the molecular

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[1] Pentacoordinated Molecules. 58. Previous paper in the series: Vollano, J. F.; Day, R. O.; Rau, D. N.; Chandrasekhar, V.; Holmes, R. R. *Inorg. Chem.* **1984**, *23*, 3153.

[2] Presented in part at the Fourth International Conference on the Organometallic and Coordination Chemistry of Germanium, Tin, and Lead, Montreal, Quebec, Aug 1983; Abstr. F-4, p 33.

[3] This work represents in part a portion of: Poutasse, Charles A., III. Ph.D. Thesis, University of Massachusetts, Amherst, MA, 1983.

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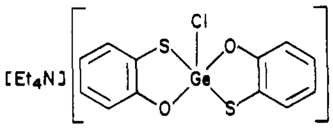

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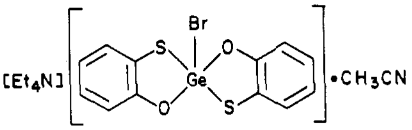

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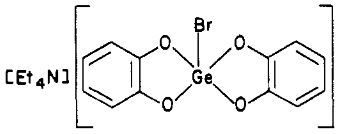

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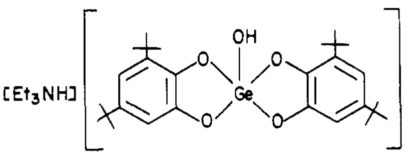

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structures of the previously prepared[12] bromo and hydroxy species, **6** and **7**, respectively. We were also able to prepare the fluoro, iodo, and hydroxy derivatives, **8**–**10**, respectively, analogous to **4** and **5** but did not obtain their X-ray structures.

By inclusion of these members **4**–**7** in the series, the ease of structural distortion relative to that obtained for five-coordinated anionic siliconates should become apparent. In addition, some comparisons with the more sparsely studied five-coordinated tin(IV) species[13,14] are possible.

Experimental Section

Acetonitrile was refluxed and distilled off of phosphorus pentoxide. Triethylamine was freshly distilled. Diethyl ether and benzene were distilled off of lithium aluminium hydride. Reagents were from commercial sources and were used without further purification. Deuterated solvents were obtained from Norell, Inc.

Proton NMR spectra were recorded on a Varian A-60 spectrometer and are referenced to tetramethylsilane. All X-ray crystallographic studies were done on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated molybdenum radiation ($\lambda(K\alpha_1) = 0.70930$ Å, $\lambda(K\alpha_2) = 0.71359$ Å) at an ambient temperature of 23 ± 2 °C. Details of the experimental and computational procedures have been described previously.[15]

Syntheses. Bis(2-hydroxy-1-benzenethiolato)germanium(IV), $(C_6H_4OS)_2Ge$ (11). *o*-Mercaptophenol (3.328 g, 26.38 mmol), synthesized as reported in the literature,[16] was stirred in benzene (60 mL), and germanium tetrachloride (2.83 g, 13.19 mmol) was added with no apparent change in the yellow solution. After refluxing for 5 h, the solution was bright red, and after an additional 13 h, the color was a deep burgundy. The solvent was removed by rotovaping to yield a red-orange product. A tan solid of **11** was obtained after washing with acetonitrile: yield 2.66 g (62%); ^{1}H NMR (CD_3CN-Me_2SO) δ 6.5–7.0 (m), 7.25 (br s), 7.35 (br s). Anal. Calcd for $C_{12}H_8O_2S_2Ge$: C, 44.91; H, 2.50. Found: C, 44.80; H, 2.53.

Tetraethylammonium Bis(2-hydroxy-1-benzenethiolato)fluorogermanate, $[(C_6H_4OS)_2GeF][Et_4N]$ (8). Bis(-2-hydroxy-1-benzenethiolato)germanium (0.675 g, 2.08 mmol) was stirred without dissolving in 40 mL of acetonitrile under nitrogen with magnesium sulfate present as a drying agent. Tetraethylammonium fluoride dihydrate (0.388 g, 2.09 mmol) was added and the solution stirred for 0.5 h. After filtering, the colorless solution was rotovaped to dryness. The white solid that formed was dissolved in 5 mL of acetonitrile, and the resultant mixture was treated with 10 mL of diethyl ether and cooled to yield colorless crystals. It was recrystallized from hot acetonitrile and dried under vacuum: yield 0.621 g (64%); mp 196–198 °C; ^{1}H NMR (CD_3CN-Me_2SO) δ 1.15 (t of t, 12 H), 3.08 (q, 8 H), 6.5–6.85 (br, 6 H), 7.1–7.35 (d, 2 H). Anal. Calcd for $C_{20}H_{28}O_2NS_2FGe$: C, 51.08; H, 6.01; N, 2.98. Found: C, 51.27; H, 6.41; N, 3.03.

Tetraethylammonium Bis(2-hydroxy-1-benzenethiolato)chlorogermanate, $[(C_6H_4OS)_2GeCl][Et_4N]$ (4). Bis(2-hydroxy-1-benzenethiolato)germanium (0.542 g, 1.669 mmol) was stirred in 40 mL of dry acetonitrile under nitrogen. Tetraethylammonium chloride (0.276 g, 1.662 mmol) was added, with the solution turning dark. The mixture was stirred and heated for 2.5 h, with the color lightening and turning purple-red. The solvent was removed by rotovaping, and some white solid was collected. A second, browner solid grew out of acetonitrile–ether solution (1:2, total volume 30 mL). Both solids melted at the same point, 191–195 °C. These were recrystallized from hot acetonitrile: mp 196–197 °C; yield 0.723 g (89%); ^{1}H NMR (CD_3CN) δ 1.2 (t of t, 12 H), 3.1 (q, 8 H), 6.4–7.0 (m, 6 H), 7.2–7.4 m, 2 H). Anal. Calcd for $C_{20}H_{28}O_2NS_2ClGe$: C, 49.36; H, 5.80; N, 2.88; Cl, 7.3. Found: C, 48.90; H, 5.80; N, 2.86; Cl, 7.14. Crystals suitable for X-ray structural analysis were grown by the slow vapor diffusion of ether into a solution of the product in acetonitrile.

Tetraethylammonium Bis(2-hydroxy-1-benzenethiolato)bromogermanate, $[(C_6H_4OS)_2GeBr][Et_4N]$ (5). Bis(2-hydroxy-1-benzenethiolato)germanium (0.711 g, 2.187 mmol) was stirred in 50 mL of dry acetonitrile under nitrogen. Tetraethylammonium bromide (0.460 g, 2.19 mmol) was added and the solution refluxed for 2 h. The solid slowly dissolved, and the reddish color gradually lightened in the course of the reaction. After filtering, the volume was reduced to 10 mL by rotovaping and a white solid precipitated from the solution. This was dried under vacuum for several hours: yield 0.8334 g (66%); mp 179.5–180.5 °C; ^{1}H NMR (CD_3CN) δ 1.15 (t of t, 12 H), 3.05 (q, 8 H), 6.5–7.4 (m, 8 H). Also, the peak for acetonitrile was stronger than that found for the normal deuterated solvent, raising the possibility that an acetonitrile molecule might have crystallized with the product. This was confirmed in the analysis. Anal. Calcd for $C_{22}H_{31}O_2N_2S_2BrGe$ (with one acetonitrile molecule): C, 46.15; H, 5.42; N, 4.90. Found: C, 46.04; H, 5.41; N, 4.70. Crystals suitable for X-ray structural analysis were grown by the slow vapor diffusion of ether into a solution of the product dissolved in acetonitrile.

Tetraethylammonium Bis(2-hydroxy-1-benzenethiolato)iodogermanate, $[(C_6H_4OS)_2GeI][Et_4N]$ (9). Bis(2-hydroxy-1-benzenethiolato)germanium (0.296 g, 0.913 mmol) was stirred in 40 mL of dry acetonitrile, partially dissolving to form a tan solution. Tetraethylammonium iodide (0.237 g, 0.922 mmol) was added and the solution refluxed for 24 h, during which time it turned orange brown and contained less solid. After the solution was allowed to stand for 3 days, a brown solid was filtered out and the solvent removed by rotovaping to yield a mixed yellow and brown solid with a wide melting range. The solid was dissolved in acetonitrile and ether added to induce crystallization. Yellow needle crystals were deposited: mp 146–152 °C; yield 0.211 g (37.4%); ^{1}H NMR (CD_3CN) δ 1.2 (t of t, 12 H), 3.1 (q, 8 H), 6.5–6.95 (m), 7.2–7.5 (8 H). The acetonitrile peak was stronger than expected for the deuterated solvent, suggesting the presence of an acetonitrile molecule with the product, which was confirmed by the analysis. Anal. Calcd for $C_{22}H_{31}O_2N_2S_2IGe$ (with one molecule of acetonitrile): C, 42.68; H, 5.04; N, 4.53. Found: C, 42.85; H, 5.22; N, 4.41. When an attempt to grow crystals was made, the only isolated solid was a white powder, indicating this product may be the least stable in the series, since it is readily decomposed in solution.

Triethylammonium Bis(2-hydroxy-1-benzenethiolato)hydroxygermanate, $[(C_6H_4OS)_2GeOH][Et_3NH]$ (10). Germanium tetrachloride (1.47 g, 6.86 mmol) was mixed in 50 mL of dry benzene under nitrogen. *o*-Mercaptophenol (1.73 g, 13.69 mmol) and triethylamine (2.77 g, 27.40 mmol) were mixed in 20 mL of benzene in a dropping funnel. Dropwise addition caused the immediate formation of a red-brown solid. The mixture was refluxed for 1 h after the addition was completed. The solvent was removed and the solid mass treated with water to dissolve triethylammonium chloride. The remaining solid was dissolved in a 1:1 mixture of acetonitrile and water and the resultant mixture refluxed briefly. The solvents were then removed and the solid recrystallized from acetonitrile and ether to yield a white-brown solid: yield 1.87 g (62%); mp 161–166 °C; ^{1}H NMR (CD_3CN) δ 1.1 (t, 9 H), 3.1 (q, 6 H), 6.5–7.3 (m, 8 H). Anal. Calcd for $C_{18}H_{25}O_3NS_2Ge$: C, 49.12; H, 5.73; N, 3.18. Found: C, 48.88; H, 5.62; N, 3.56.

X-ray Crystallographic Study. $[(C_6H_4OS)_2GeCl][NEt_4]$ (4). A colorless crystal (0.10 × 0.40 × 0.40 mm), which was cut from a larger lath and mounted inside of a sealed thin-walled glass capillary as a precaution against moisture sensitivity, was used for the X-ray study.

Crystal data: $C_{20}H_{28}O_2NS_2GeCl$ (4), monoclinic space group *Cc* [C_s^4-No. 9],[17] $a = 10.869$ (3) Å, $b = 12.852$ (4) Å, $c = 16.798$ (4) Å, β

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= 103.00 (2)°, $Z = 4$, $\mu_{\mathrm{Mo}\,K\alpha} = 1.724$ mm^{-1}; 1988 independent reflections ($+h,+k,\pm l$) measured with the θ–2θ scan mode for $2° \le 2\theta_{\mathrm{Mo}\,K\alpha} \le 50°$; no corrections made for absorption.

The structure was solved by using standard Patterson and difference Fourier techniques and was refined by using full-matrix least squares.[18] The 27 non-hydrogen atoms were refined anisotropically. The eight aromatic hydrogen atoms and the eight methylene hydrogen atoms were included in the refinement as fixed isotropic scatterers with calculated coordinates that were updated as refinement converged so that the final C–H bond lengths were 0.98 Å. The 12 methyl hydrogen atoms could not be located in difference Fourier syntheses and were omitted from the refinement. The final agreement factors[19] were $R = 0.037$ and $R_w = 0.046$ for the 1738 reflections having $I \ge 2\sigma_I$.

[$(C_6H_4OS)_2GeBr$][NEt_4]·CH_3CN (5). Colorless, boomerang-shaped crystals of **5**, grown from CH_3CN–Et_2O are very air/moisture sensitive. A nearly cube-shaped crystal (0.26 × 0.30 × 0.32 mm), which was cut from a larger one and mounted inside of a sealed thin-walled glass capillary, proved to be stable throughout the X-ray study.

Crystal data: $C_{22}H_{31}O_2N_2S_2GeBr$ (**5**), monoclinic space group $P2_1$ [C_2^2-No. 4],[20] $a = 12.345$ (2) Å, $b = 27.800$ (5) Å, $c = 7.779$ (1) Å, $\beta = 104.54$ (1)°, $Z = 4$, $\mu_{\mathrm{Mo}\,K\alpha} = 3.07$ mm^{-1}; 3022 independent reflections ($+h,+k,\pm l$) measured with the θ–2θ scan mode for $2° \le 2\theta_{\mathrm{Mo}\,K\alpha} \le 43°$; no corrections made for absorption.

The structure was solved and refined by using the same techniques described for **4**. Due to the paucity of data and the possibility that these atoms would be poorly defined, the 22 non-hydrogen atoms comprising both the ethyl groups of the two independent cations and the two independent acetonitrile molecules were refined isotropically. The remaining 38 independent non-hydrogen atoms were refined anisotropically. Hydrogen atoms were omitted from the refinement. Although there is an apparent pseudo-centering operation ($\sim {}^1/_2 + x$, ${}^1/_4 + y$, ${}^1/_2 + z$) in the cell, no unusual correlations were observed during the refinement. The final agreement factors[19] were $R = 0.051$ and $R_w = 0.065$ for the 2513 reflections having $I \ge 2\theta_I$.

[$(C_6H_4O_2)_2GeBr$][NEt_4] (6). Crystals of this compound are very air/moisture sensitive. A 0.30 × 0.33 × 0.33 mm crystal, which was cut from a colorless lath and mounted inside of a sealed thin-walled capillary, was stable throughout the X-ray study.

Crystal data: $C_{20}H_{28}O_4NGeBr$, uniquely determined monoclinic space group $P2_1/c$ [C_{2h}^5-No. 14],[21] $a = 11.144$ (1) Å, $b = 10.916$ (2) Å, $c = 18.293$ (2) Å, $\beta = 96.89$ (1)°, $Z = 4$, $\mu_{\mathrm{Mo}\,K\alpha} = 3.41$ mm^{-1}; 3875 independent reflections ($+h,+k,\pm l$) measured under the same conditions as described for **4**; no corrections made for absorption.

The structure was solved and refined by use of the same techniques that were described for **4**. For the anion, the eight hydrogen atoms were included in the refinement as fixed isotropic scatterers, while the 18 non-hydrogen atoms were refined anisotropically. The cation is disordered and was described in terms of two conformations (one with 0.61 occupancy and one with 0.39 occupancy based on difference Fourier peak heights) having three atoms (N, C16, and C18—full occupancy) in common. These three common atoms were refined anisotropically, while atoms having partial occupancy were refined isotropically. Hydrogen atoms of the cation were omitted. The final agreement factors were $R = 0.059$ and $R_w = 0.070$ for the 2597 reflections having $I \ge 2\theta_I$.

[$(C_{14}H_{20}O_2)_2GeOH$][Et_3NH] (7). A colorless crystal (0.23 × 0.30 × 0.32 mm), which was cut from a colorless striated rod and mounted inside of a sealed thin-walled glass capillary as a precaution against moisture sensitivity, was used for the X-ray study.

Crystal data: $C_{34}H_{57}O_5NGe$, orthorhombic space group $Pna2_1$ [C_{2v}^9-No. 33],[22] $a = 21.415$ (5) Å, $b = 16.279$ (5) Å, $c = 10.297$ (3) Å, $Z = 4$, $\mu_{\mathrm{Mo}\,K\alpha} = 0.944$ mm^{-1}; 3347 independent reflections ($+h,+k,+l$) measured under the same conditions as described for **4**; no corrections made for absorption.

The structure was solved and refind by use of the same techniques that were described for **4**. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were omitted from the refinement. The final agreement

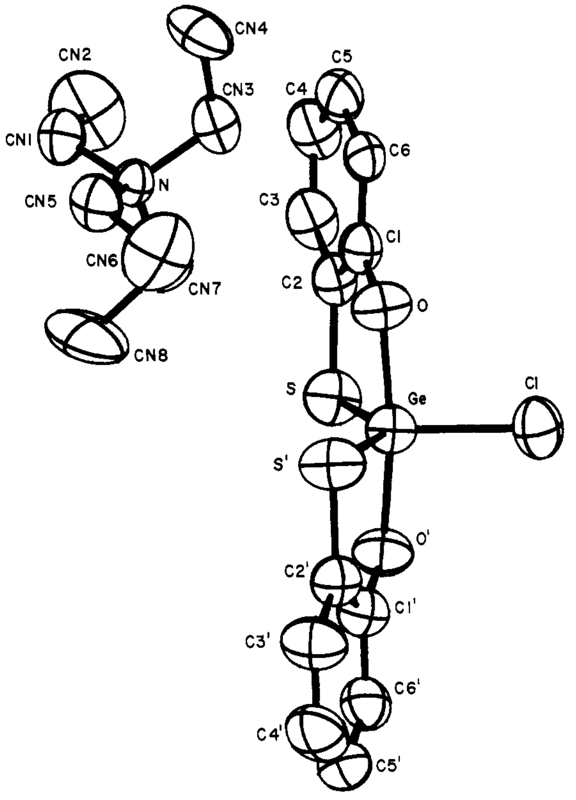

Figure 1. ORTEP plot of [$(C_6H_4OS)_2GeCl$][NEt_4] (**4**) with thermal ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for purposes of clarity.

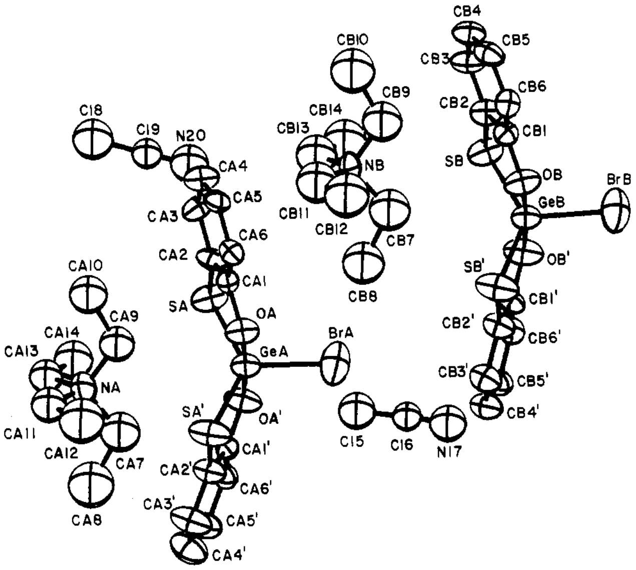

Figure 2. ORTEP plot of the contents of the asymmetric unit for [$(C_6H_4OS)_2GeBr$][NEt_4]·CH_3CN (**5**) with thermal ellipsoids at the 50% probability level.

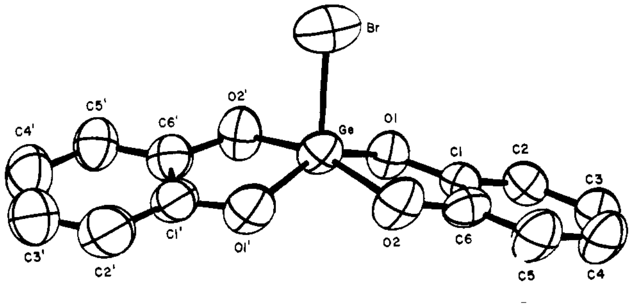

Figure 3. ORTEP plot of the anion of [$(C_6H_4O_2)_2GeBr$][NEt_4] (**6**) with thermal ellipsoids at the 50% probability level.

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(17) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. I, p 89.

(18) 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: "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 72–98. Real and imaginary dispersion corrections for Ge, Cl, Br, and O were taken from the same source, pp 149–150.

(19) $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. These values are for the configuration having the lowest R_w, for the acentric space groups.

(20) Reference 17, p 79.

(21) Reference 17, p 99.

(22) Reference 17, p 119.

Table I. Atomic Coordinates in Crystalline $[(C_6H_4SO)_2GeCl][NEt_4]$ (4)[a]

atom[b]	coordinates 10^4x	10^4y	10^4z
Ge	10000[c]	7487.0 (6)	7500[c]
Cl	10950 (2)	6320 (2)	6897 (2)
S	10890 (2)	7675 (2)	8826 (1)
S'	8372 (2)	8248 (2)	6660 (1)
O	8853 (5)	6510 (4)	7775 (3)
O'	11050 (5)	8600 (4)	7315 (4)
N	5178 (5)	7403 (4)	8409 (4)
C1	9086 (6)	6178 (5)	8554 (4)
C2	10021 (7)	6649 (5)	9146 (4)
C3	10251 (8)	6305 (6)	9951 (4)
C4	9538 (9)	5524 (6)	10165 (5)
C5	8609 (9)	5047 (6)	9596 (6)
C6	8382 (7)	5369 (5)	8766 (5)
C1'	10572 (7)	9271 (7)	6706 (4)
C2'	9280 (7)	9218 (6)	6324 (4)
C3'	8781 (8)	9925 (7)	5704 (5)
C4'	9529 (10)	10664 (7)	5477 (7)
C5'	10825 (10)	10725 (7)	5850 (6)
C6'	11329 (8)	10029 (6)	6475 (5)
CN1	5006 (9)	7577 (6)	9260 (5)
CN2	6060 (14)	7155 (11)	9938 (7)
CN3	5287 (8)	6260 (6)	8238 (5)
CN4	4141 (9)	5608 (6)	8320 (7)
CN5	4043 (8)	7871 (7)	7824 (5)
CN6	4054 (13)	7804 (12)	6937 (7)
CN7	6408 (7)	7896 (7)	8314 (6)
CN8	6458 (10)	9086 (8)	8458 (9)

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

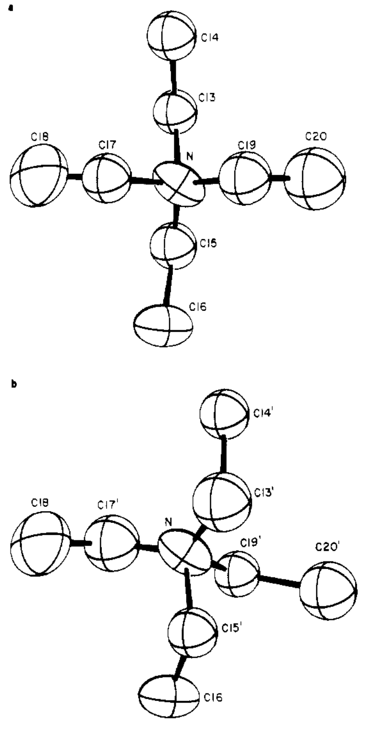

Figure 4. ORTEP plots showing the two conformations for the disordered cation in $[(C_6H_4O_2)_2GeBr][NEt_4]$ (**6**): (a) 61% occupancy; (b) 39% occupancy. Atoms N, C16, and C18 (full occupancy) are common to both conformations.

factors were $R = 0.061$ and $R_w = 0.074$ for the 2450 reflections having $I \geq 2\sigma_I$.

Table II. Atomic Coordinates in Crystalline $[(C_6H_4OS)_2GeBr][NEt_4]\cdot CH_3CN$ (5)[a]

atom[b]	coordinates 10^4x	10^4y	10^4z
BrA	9817 (2)	7110[c]	5528 (3)
BrB	4951 (2)	4636 (1)	10043 (4)
GeA	9951 (1)	7952 (1)	5453 (2)
GeB	5197 (1)	5472 (1)	9969 (3)
SA	8351 (3)	8334 (2)	5326 (5)
SA'	11635 (3)	8251 (2)	5500 (5)
SB	3639 (3)	5897 (2)	9878 (5)
SB'	6921 (3)	5707 (2)	10015 (5)
OA	9625 (7)	7961 (4)	2926 (10)
OA'	10302 (7)	8008 (4)	7972 (10)
OB	4853 (7)	5484 (4)	7440 (11)
OB'	5533 (7)	5526 (4)	12491 (12)
CA1	8591 (10)	8109 (4)	2050 (17)
CA2	7869 (11)	8291 (6)	2977 (17)
CA3	6790 (12)	8442 (6)	2077 (20)
CA4	6445 (12)	8391 (6)	272 (20)
CA5	7187 (10)	8211 (5)	−686 (18)
CA6	8244 (11)	8058 (5)	224 (16)
CA1'	11329 (11)	8141 (5)	8790 (17)
CA2'	12096 (11)	8279 (6)	7826 (18)
CA3'	13150 (13)	8440 (7)	8714 (22)
CA4'	13450 (15)	8477 (7)	10575 (22)
CA5'	12695 (12)	8340 (6)	11504 (19)
CA6'	11637 (11)	8180 (5)	10680 (18)
CB1	3844 (11)	5652 (5)	6584 (17)
CB2	3147 (11)	5869 (5)	7552 (17)
CB3	2098 (11)	6053 (6)	6666 (19)
CB4	1759 (11)	6026 (6)	4811 (20)
CB5	2458 (12)	5804 (6)	3847 (19)
CB6	3473 (12)	5618 (5)	4741 (18)
CB1'	6609 (10)	5621 (5)	13302 (17)
CB2'	7392 (11)	5711 (6)	12349 (17)
CB3'	8514 (12)	5822 (6)	13255 (19)
CB4'	8834 (12)	5832 (6)	15056 (20)
CB5'	8046 (12)	5746 (6)	16001 (19)
CB6'	6934 (11)	5646 (5)	15173 (18)
NA	9594 (12)	9572 (5)	10543 (21)
NB	5100 (11)	7079 (5)	4967 (19)
CA7	10394 (19)	9222 (9)	11817 (31)
CA8	11453 (24)	9489 (10)	13091 (39)
CA9	8723 (16)	9260 (7)	9386 (26)
CA10	7817 (18)	9533 (8)	7957 (29)
CA11	10234 (16)	9871 (8)	9553 (26)
CA12	10846 (24)	9528 (10)	8335 (37)
CA13	9109 (15)	9954 (7)	11644 (25)
CA14	8444 (18)	9725 (8)	12832 (29)
CB7	5868 (19)	6701 (9)	6211 (32)
CB8	6937 (20)	6941 (9)	7488 (34)
CB9	4175 (19)	6779 (9)	3903 (31)
CB10	3233 (21)	7063 (10)	2532 (35)
CB11	5706 (19)	7364 (8)	3959 (30)
CB12	6269 (22)	7050 (10)	2633 (35)
CB13	4616 (18)	7425 (9)	6046 (30)
CB14	3991 (21)	7187 (10)	7320 (33)
C15	9951 (15)	6972 (8)	10563 (26)
C16	10128 (13)	6486 (7)	10185 (21)
N17	10312 (13)	6090 (7)	9955 (22)
C18	4637 (19)	9526 (9)	4825 (32)
C19	4869 (13)	9017 (7)	5217 (21)
N20	5035 (14)	8611 (7)	5489 (23)

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

Results

The atom-labeling scheme for **4** is shown in the ORTEP plot of Figure 1, while atomic coordinates are given in Table I. The corresponding information for **5** is given in Figure 2 and in Table II. Selected bond lengths and angles for both compounds appear in Table III.

For **6**, the atom-labeling scheme is shown in the ORTEP plots of Figures 3 and 4. Atomic coordinates and selected bond lengths, angles, and contacts are given in Tables IV and VI, respectively. For **7**, the corresponding information is given in Figure 5 and in Tables V and VII. Anisotropic thermal parameters, hydrogen atom parameters, additional bond lengths and angles, and deviations from selected least-squares mean planes are provided as supplementary material.

Table III. Bond Lengths (Å) and Bond Angles (deg) Involving Germanium for 4 (X = Cl) and 5 (X = Br)

	4	5A	5B
	Lengths		
Ge–X	2.194 (2)	2.350 (3)	2.348 (3)
Ge–O	1.898 (5)	1.905 (8)	1.906 (8)
Ge–O′	1.899 (5)	1.904 (8)	1.906 (9)
Ge–S	2.233 (2)	2.221 (4)	2.242 (4)
Ge–S′	2.226 (2)	2.231 (4)	2.218 (4)
	Angles		
O–Ge–O′	171.9 (3)	174.5 (5)	174.6 (6)
S–Ge–S′	133.5 (1)	129.7 (2)	131.1 (2)
X–Ge–S	113.0 (1)	114.2 (2)	114.0 (2)
X–Ge–S′	113.4 (1)	116.2 (2)	114.8 (2)
O–Ge–X	93.6 (2)	92.3 (3)	92.6 (4)
O′–Ge–X	94.4 (2)	93.1 (4)	92.7 (4)
O–Ge–S	89.4 (2)	89.6 (3)	89.5 (3)
O′–Ge–S′	89.2 (2)	89.0 (3)	90.0 (3)
O–Ge–S′	88.4 (2)	88.1 (3)	88.6 (3)
O′–Ge–S	86.6 (2)	88.7 (3)	87.4 (3)

Table IV. Atomic Coordinates in Crystalline $[(C_6H_4O_2)_2GeBr][NEt_4]$ (6)[a]

	coordinates		
atom[b]	10^4x	10^4y	10^4z
Br	1927.7 (8)	3569.1 (9)	3797.2 (5)
Ge	2685.6 (6)	5152.9 (7)	3140.6 (4)
O1′	2192 (5)	6591 (5)	3501 (3)
O2′	4129 (4)	5384 (4)	3720 (3)
O2	1435 (4)	5346 (5)	2387 (3)
O1	3554 (4)	4474 (4)	2454 (2)
C1	2852 (6)	4306 (6)	1808 (3)
C2	3227 (7)	3722 (7)	1208 (4)
C3	2421 (9)	3595 (7)	568 (4)
C4	1285 (8)	4059 (9)	536 (4)
C5	894 (7)	4666 (8)	1146 (4)
C6	1687 (6)	4774 (7)	1769 (4)
C1′	3003 (7)	7005 (7)	4062 (4)
C2′	2821 (10)	8031 (9)	4490 (5)
C3′	3725 (12)	8330 (9)	5054 (5)
C4′	4749 (9)	7653 (9)	5182 (5)
C5′	4928 (7)	6647 (7)	4757 (4)
C6′	4041 (7)	6327 (7)	4188 (4)
N	−2383 (5)	4644 (6)	3094 (3)
C13	−1183 (11)	5191 (11)	2859 (7)
C13′	−2201 (27)	5592 (28)	3616 (16)
C14	−956 (13)	6601 (14)	2998 (9)
C14′	−822 (21)	6285 (20)	3441 (13)
C15	−2468 (12)	3401 (13)	2852 (7)
C15′	−3559 (20)	3950 (20)	3335 (11)
C16	−3827 (8)	2791 (8)	2949 (5)
C17	−3483 (13)	5506 (13)	2665 (8)
C17′	−2349 (23)	4669 (24)	2279 (14)
C18	−3504 (10)	5465 (12)	1883 (7)
C19	−2485 (15)	4968 (15)	3931 (9)
C19′	−1381 (17)	3493 (18)	3256 (10)
C20	−1463 (18)	4261 (20)	4381 (10)
C20′	−1228 (23)	3181 (26)	4184 (14)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figures 3 and 4.

Table V. Atomic Coordinates in Crystalline $[(C_{14}H_{20}O_2)_2GeOH][Et_3NH]$ (7)[a]

	coordinates		
atom[b]	10^4x	10^4y	10^4z
Ge	9585.8 (4)	9695.4 (5)	7500[c]
O1	9770 (3)	10591 (4)	8565 (7)
O2	8825 (3)	10167 (4)	7216 (6)
O1′	10137 (3)	9107 (4)	8530 (7)
O2′	9184 (3)	8719 (4)	7167 (7)
O3	10071 (3)	9946 (5)	6172 (7)
C1	9303 (5)	11172 (6)	8500 (10)
C2	8784 (4)	10921 (5)	7778 (9)
C3	8272 (4)	11438 (5)	7676 (11)
C4	8298 (6)	12198 (6)	8336 (11)
C5	8819 (6)	12430 (6)	9047 (10)
C6	9337 (5)	11896 (6)	9163 (10)
C31	7690 (5)	11156 (7)	6860 (12)
C32	7905 (6)	10990 (9)	5444 (13)
C33	7421 (5)	10334 (7)	7393 (22)
C34	7147 (6)	11835 (9)	6914 (14)
C51	8801 (7)	13263 (7)	9819 (12)
C52	9425 (10)	13556 (10)	10114 (26)
C53	8501 (11)	13898 (7)	9000 (21)
C54	8469 (10)	13171 (9)	11050 (17)
C1′	10017 (4)	8286 (5)	8473 (10)
C2′	9488 (4)	8073 (5)	7747 (9)
C3′	9286 (4)	7256 (5)	7727 (9)
C4′	9645 (5)	6695 (6)	8371 (11)
C5′	10180 (5)	6893 (6)	9070 (11)
C6′	10373 (4)	7711 (6)	9121 (10)
C31′	8681 (5)	7033 (7)	6996 (13)
C32′	8729 (8)	7325 (10)	5556 (14)
C33′	8548 (6)	6110 (6)	7073 (17)
C34′	8131 (4)	7501 (7)	7635 (27)
C51′	10517 (6)	6176 (8)	9807 (12)
C52′	11176 (8)	6500 (10)	10375 (22)
C53′	10650 (7)	5461 (7)	8921 (17)
C54′	10132 (7)	5922 (8)	10978 (15)
N	11219 (3)	10550 (5)	6724 (9)
C7	11513 (7)	10626 (14)	5428 (21)
C8	12177 (8)	10858 (11)	5531 (24)
C9	11145 (7)	11296 (12)	7518 (31)
C10	10756 (6)	11978 (8)	6730 (16)
C11	11526 (9)	9908 (10)	7440 (35)
C12	11585 (6)	9086 (7)	6761 (18)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 5. [c] Fixed.

Table VI. Selected Bond Lengths (Å) and Bond Angles (deg) for $[(C_6H_4O_2)_2GeBr][NEt_4]$ (6)[a,b]

	Lengths		
Ge–O1	1.832 (4)	O1–C1	1.349 (7)
Ge–O1′	1.813 (5)	O1′–C1′	1.361 (9)
Ge–O2	1.851 (4)	O2–C6	1.351 (8)
Ge–O2′	1.834 (4)	O2′–C6′	1.350 (8)
Ge–Br	2.321 (1)		
	Angles		
O2–Ge–O2′	160.8 (2)	Br–Ge–O2′	98.7 (2)
O1–Ge–O1′	143.9 (2)	Ge–O1–C1	110.9 (4)
O1–Ge–O2	87.0 (2)	Ge–O1′–C1′	111.0 (4)
O1′–Ge–O2′	87.4 (2)	Ge–O2–C6	111.0 (4)
O1′–Ge–O2	86.4 (2)	Ge–O2′–C6′	110.2 (4)
O1–Ge–O2′	87.3 (2)	O1–C1–C6	115.8 (6)
Br–Ge–O1	108.0 (1)	O1′–C1′–C6′	114.7 (7)
Br–Ge–O1′	108.2 (2)	O2–C6–C1	114.2 (6)
Br–Ge–O2	100.5 (2)	O2′–C6′–C1′	115.4 (7)

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

Discussion

Structural Features. The anionic germanium complexes **4–6** have a pseudo-2-fold axis that is coincident with the Ge–halogen bond. To facilitate the examination of this pseudosymmetry, atoms have been labeled so that primed atoms are psuedo-2-fold related to unprimed ones. As can be seen in Figure 2 and in Table III, the two independent molecules for **5** are nearly identical.

The geometry about the Ge atom for both mixed-ligand-containing compounds **4** and **5** lies between a trigonal bipyramid (TBP) with the oxygen atoms in axial positions and a rectangular pyramid (RP) with basal chalcogen atoms and an apical halogen atom. In terms of the Berry pseudorotation coordinate, the dihedral angle method[6,7,23] shows that **4** is displaced 34.5% (34.2% using unit vectors) from the TBP to the RP. In the case of **5**, these values are 25.6% average (23.6% using unit vectors) and 27.4% average (26.2% using unit vectors) for anions A and B, respectively.

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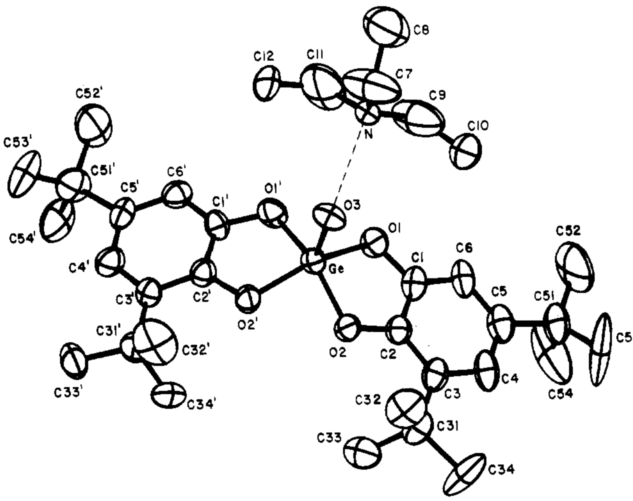


Figure 5. ORTEP plot of $[(C_{14}H_{20}O_2)_2GeOH][Et_3NH]$ (7) with thermal ellipsoids at the 50% probability level. Hydrogen bonding between the cation and the anion is indicated by the dotted line.

Table VII. Selected Bond Lengths (Å), Bond Angles (deg), and Nonbonded Contacts (Å) for $[(C_{14}H_{20}O_2)_2GeOH][Et_3NH]$ (7)[a,b]

	Lengths		
Ge–O1	1.866 (6)	O1–C1	1.38 (1)
Ge–O1′	1.853 (7)	O2′–C2′	1.37 (1)
Ge–O2	1.825 (6)	O2–C2	1.36 (1)
Ge–O2′	1.839 (6)	O1′–C1′	1.36 (1)
Ge–O3	1.766 (7)	O3- - -N	2.71 (1)
	Angles		
O1–Ge–O2′	152.0 (3)	Ge–O2–C2	111.6 (5)
O1′–Ge–O2	151.3 (3)	Ge–O1′–C1′	111.3 (6)
O1–Ge–O2	87.4 (3)	Ge–O2′–C2′	111.0 (5)
O1′–Ge–O2′	87.6 (3)	O1–C1–C2	113.7 (8)
O1–Ge–O1′	86.2 (3)	O1′–C1′–C2′	114.7 (8)
O2–Ge–O2′	85.1 (3)	O2–C2–C1	116.0 (8)
O3–Ge–O1	98.6 (3)	O2′–C2′–C1′	115.2 (7)
O3–Ge–O1′	100.9 (3)	Ge–O3- - -N	117.1 (4)
O3–Ge–O2	107.7 (3)	C7–N- - -O3	103.1 (7)
O3–Ge–O2′	109.3 (3)	C9–N- - -O3	108.6 (7)
Ge–O1–C1	110.8 (6)	C11–N- - -O3	105.0 (7)

[a] Numbers in parentheses are estimated standard deviations.
[b] Atoms are labeled to agree with Figure 5.

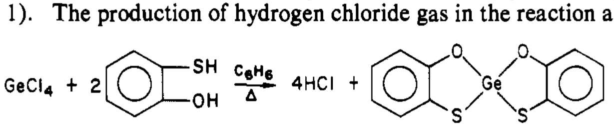
The molecular geometry about the Ge atom in **6** lies on the coordinate connecting the TBP (with O2 and O2′ axially positioned) to the RP having the Br atom in the apical position. In terms of the Berry coordinate,[24] the geometry is displaced 62.7% (70.4% using unit vectors) from the TBP toward the RP.

The ORTEP plot of Figure 5 shows that **7** has a pseudo mirror plane that would ideally contain Ge, O3, N, C7, and C8. To facilitate the examination of this pseudosymmetry, atoms of the anion are labeled so that the primed ones go into the unprimed ones by the pseudo mirror plane.

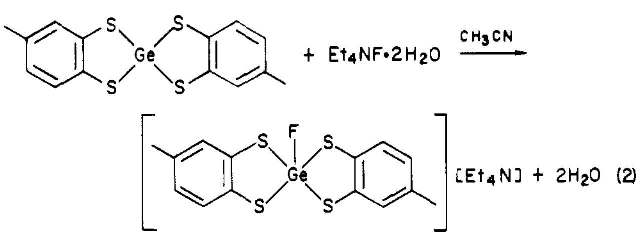
Although hydrogen atoms could not be located, analysis of the non-hydrogen atom geometry indicates that there is a hydrogen bond between the N–H hydrogen atom of the cation and the hydroxyl oxygen atom of the anion. The angles C7–N- - -O3, C9–N- - -O3, and C11–N- - -O3 are 103.1 (7), 108.6 (7), and 105.0 (7)°, respectively. The nearly tetrahedral values of these angles indicate that the N–H hydrogen atom is directed toward O3. The Ge–O3- - -N angle of 117.1 (4)° also suggests that the hydroxyl oxygen atom has a lone pair directed approximately toward the NH hydrogen atom. The sum of the van der Waals radii for N and O is 3.0 Å.[25] For the H atom positioned between N and O3, the combined sum of the N–H bond length and the van der Waals radii of H and O is 3.4 Å. The observed distance between N and O3 of only 2.71 (1) Å indicates a reasonably strong hydrogen-bonding interaction.

The geometry about the Ge atoms for **7** is essentially that of a rectangular pyramid, with the hydroxyl oxygen atom occupying the apical position. In terms of the distortion from a TBP toward a RP, the dihedral angle method gives average percentages of 96.0% and 95.7%, the latter using unit vectors. The trans basal angles of 152.0 (3) and 151.3 (3)° are within 3 standard deviations of each other, and the atoms comprising the basal plane (O1, O2, O1′, O2′) are coplanar to within ±0.004 Å. The germanium atom is displaced 0.452 Å out of this plane in the direction of the apical oxygen atom. Deviations from the idealized RP geometry seem to follow the constraints of the pseudo mirror symmetry, rather than the 2-fold symmetry that would be required for distortion along the Berry coordinate toward the trigonal bipyramid. The distortion from the RP may be due to the hydrogen-bonding interaction since the hydroxyl oxygen atom is tipped toward the cation with respect to the basal plane. This tipping can be seen in the apical to basal angles between oxygen atoms that are 100.9 (3) and 98.6 (3)° on the side of the RP that faces the cation and 109.3 (3) and 107.7 (3)° on the opposite side.

Synthetic Aspects. Mercaptophenol reacted smoothly with germanium tetrachloride in boiling benzene to yield the previously unknown bis(mercaptophenol)germanium(IV) compound **11** (eq 1). The production of hydrogen chloride gas in the reaction and the color changes in solution, yellow to red to burgandy, allow the end point of the reaction to be established. In reaction with tetraethylammonium halides, **11** forms five-coordinated complexes $[(C_6H_4OS)_2GeX][Et_4N]$ with relative ease with all of the halides, F (**8**), Cl (**4**), Br (**5**), and I (**9**). With the germanium dicatecholate $(C_6H_4O_2)_2Ge\cdot 2H_2O$, pentacoordinated complexes form with fluoride, chloride, and bromide salts.[12] In contrast, the bis(toluenedithiolato)germanium compound $(C_7H_6S_2)_2Ge$ formed a complex only with fluoride[12] (eq 2). Although formation of the chloro analogue in solution was indicated, attempts to isolate the five-coordinated product resulted in the redeposition of the starting bis(dithiolato) compound.[12] In the case of dicatecholate complexes, $[(C_6H_4O_2)_2GeX][Et_4N]$, hydrolytic stability decreases in the order F > Cl > Br.[12]



11 (1)



The mixed-ligand germanium derivatives **4**, **5**, **8**, and **9** are rare examples of anionic pentacoordinated complexes of main-group 4 elements containing a spirocyclic framework. None are known for silicon, and only one recent example is known for tin(IV), $[(C_6H_4OS)_2SnCl][Et_4N]$.[26]

It is interesting that the mixed-ligand compound, bis(thiaethanediol)germanium(IV), does not add halides to form any pentacoordinated complexes that could be isolated.[27] This suggests that the greater electronegativity associated with a benzene ring relative to the ethylene group[28] may be effective in providing

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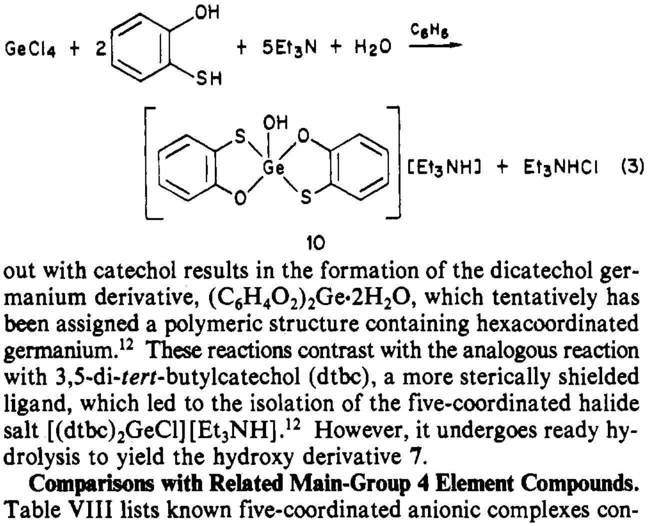
Table VIII. Structural Distortion for Five-Coordinated Halogen-Containing Main-Group 4 Compounds

compd	%(TBP → RP)[a]	ref
$[Et_4N][(C_6H_4OS)_2GeBr]\cdot CH_3CN$ (**5**)	23.6 (A), 26.2 (B)[b]	this work
$[Et_4N][(C_6H_4OS)_2GeCl]$ (**4**)	34.2	this work
$[Ph_3PMe][(C_7H_7S_2)_2GeF]\cdot CH_3CN$ (**3**)	40.3	11
$[Et_4N][(C_6H_4O_2)_2GeBr]$ (**6**)	70.4	this work
$[Et_4N][(C_6H_4O_2)_2GeF]$ (**2**)	80.6	11
$[Et_4N][(C_6H_4O_2)_2GeCl]$ (**1**)	90.7	10
$[Et_3NH][(dtbc)_2GeOH]$[c] (**7**)	95.7	this work
$[Et_4N][(C_6H_4O_2)_2SiF]$ (**12**)	68.7, 52.8[b]	29
$[Et_4N][(C_6H_4OS)_2SnCl]$ (**13**)	38.0	26
$[Me_4N][(C_7H_6S_2)_2SnCl]$[d] (**14**)	76.9	15, 30
$[MePPh_3][(C_7H_6S_2)_2SnBr]$[d] (**15**)	94.2	31

[a] The percent displacement from the ideal trigonal bipyramid toward the rectangular pyramid is calculated from unit bond distances based on the dihedral angle method.[6] The θ value for the "ideal" rectangular pyramid used in the calculation of the percent displacement is 150°. [b] Two independent molecules per unit cell. [c] The ligand dtbc is 3,5-di-*tert*-butylcatechol. [d] The ligand $C_7H_6S_2$ is toluene-3,4-dithiol.

increased electron withdrawal from the germanium center via the coordinating atoms and hence account for the lack of the mixed-ligand species $(C_2H_4OS)_2Ge$ to add a halide ion base. The electronegativity effect also may be partly responsible for the lack of complex formation with germanium containing the less electronegative tetrathia unit with anything but the least basic fluoride ion.

Worth pointing out also is the reaction of $GeCl_4$ with mercaptophenol in the presence of Et_3N in benzene solution, which upon washing with water to remove Et_3NHCl yields the hydroxygermanate **10** (eq 3). This same reaction sequence carried out with catechol results in the formation of the dicatechol germanium derivative, $(C_6H_4O_2)_2Ge\cdot 2H_2O$, which tentatively has been assigned a polymeric structure containing hexacoordinated germanium.[12] These reactions contrast with the analogous reaction with 3,5-di-*tert*-butylcatechol (dtbc), a more sterically shielded ligand, which led to the isolation of the five-coordinated halide salt $[(dtbc)_2GeCl][Et_3NH]$.[12] However, it undergoes ready hydrolysis to yield the hydroxy derivative **7**.



(3)

10

Comparisons with Related Main-Group 4 Element Compounds. Table VIII lists known five-coordinated anionic complexes containing a spirocyclic system attached to a main-group 4 element and a halogen atom as the fifth ligand. The progressively increasing structural distortion toward the RP from the TP observed as one descends the list of germanium compounds is in accord with the general structural trends found for phosphoranes.[6,7,32] When the ring atoms in a spirocyclic system in any one five-membered ring are different, even though ring unsaturation is present, the structure tends to be near the trigonal bipyramid. This is a consequence of the disparity in electronegativity between the ring atoms and the preference for the positioning of the more electronegative ring atom in the axial site of the trigonal bipyramid.[33] The dominant factor in stabilizing the inherently less stable rectangular pyramid for germanium as with phosphorus[32] is the presence of two unsaturated five-membered rings with like atoms in any one ring. The influence of the size or electronegativity of the halogen ligand is not apparent here.

The most rectangular pyramidal germanium compound **7** contains an apical hydroxyl group that is hydrogen bonded to the triethylammonium cation (Figure 5). This adds to the steric bulk at this position and may be partly responsible for causing the appearance of the least distorted RP through steric repulsion with the basal *tert*-butyl substituents.

In line with a reduced central atom electronegativity going down the group 4 series, the tendence to form structures further displaced toward the RP for a comparable set of ligands generally increases from Si to Ge to Sn, at least with the examples of Table VIII. This is found on comparison of the degree of distortion between $[Et_4N][(C_6H_4O_2)_2SiF]$ (**12**) and $[Et_4N][(C_6H_4O_2)_2GeF]$ (**2**) and a comparison of the dithiolato derivatives of germanium and tin, i.e., the distortion of $[MePPh_3][(C_7H_6S_2)_2GeF]\cdot CH_3CN$ (**3**) relative to that in the related chloro and bromo tin derivatives **14** and **15**, as well as between $[Et_4N][(C_6H_4OS)_2GeCl]$ (**4**) and $[Et_4N][(C_6H_4OS)_2SnCl]$ (**13**). These data support an earlier indication of this structural trend.[11] The reduced bond pair repulsion effects, in terms of VSEPR theory,[34] as one goes from Si to Ge to Sn, should act to stabilize the RP relative to the inherently more stable TBP. The implication is that anionic pentacoordinated germanium compounds should be more stereochemically nonrigid than analogous silicon derivatives and that related tin derivatives should be even more nonrigid than germanium species.

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Supplementary Material Available: Listings of fixed parameters for hydrogen atoms (Tables A and H), thermal parameters (Tables B, C, G, and K), least-squares planes (Table D), additional bond lengths and angles (Tables E, F, I, and L), deviations from least-squares mean planes (Tables J and M), and observed and calculated structure factors (52 pages). Ordering information is given on any current masthead page.

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