pendent F⋯F vibrational amplitudes (F_2⋯F_e, F_2⋯F_e', and F_2⋯F_a') was obtained. This allows a rough estimate of the torsional force constant f_r = 0.03 (+0.04, −0.015) mdyn Å. With the assumption of a V_6 cosine potential the barrier to internal rotation is estimated to V_6 = 0.24 (+0.32, −0.12) kcal mol⁻¹. All spectroscopic calculations were performed with the program NORCOR.[28]

(28) D. Christen, *J. Mol. Struct.*, **48**, 101 (1978).

Contribution from the Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003

Molecular Structure of Fluoro Derivatives of Anionic Pentacoordinated Germanium. A New Geometrical Form for Germanium[1,2]

ROBERTA O. DAY, JOAN M. HOLMES, ARJUN C. SAU, and ROBERT R. HOLMES*

The X-ray structures of tetraethylammonium bis(1,2-benzenediolato)fluorogermanate, [(C₂H₅)₄N]⁺[(C₆H₄O₂)₂GeF]⁻ (**3**), and the related monosolvate of methyltriphenylphosphonium bis(4-methyl-1,2-benzenedithiolato)fluorogermanate, [(CH₃)PPh₃]⁺[(C₇H₆S₂)₂GeF]⁻·CH₃CN (**4**), lie along the Berry C_{2v} coordinate connecting the idealized trigonal bipyramid with the rectangular pyramid. The structure of **3** is placed about 81% along this coordinate toward the rectangular pyramid and that for **4** is about 40% along this coordinate. **3** crystallizes in the monoclinic space group $P2_1/c$ with a = 12.886 (2) Å, b = 14.870 (2) Å, c = 10.912 (1) Å, β = 100.29 (1)°, and Z = 4. **4** crystallizes in the monoclinic space group $P2_1/n$ with a = 17.108 (6) Å, b = 10.566 (3) Å, c = 20.630 (6) Å, β = 114.01 (2)°, and Z = 4. The final conventional unweighted residuals were 0.035 and 0.058 for **3** and **4**, respectively. The greater displacement of the pentacoordinated oxa compound **3** toward the RP is rationalized in terms of reduced electron-pair-repulsion effects.

Introduction

Most prevalent among pentacoordinated compounds of main group 4 elements are those of tin.[3] However, most of these contain relatively weak inter- or intramolecular tin dative bonds. A few examples are known that are anionic derivatives which have been characterized structurally as trigonal bipyramidal.[4-7] Recently, we reported[8] the first example of a discrete pentacoordinated anionic tin(IV) compound that has a rectangular pyramidal geometry (**1**). As observed in our
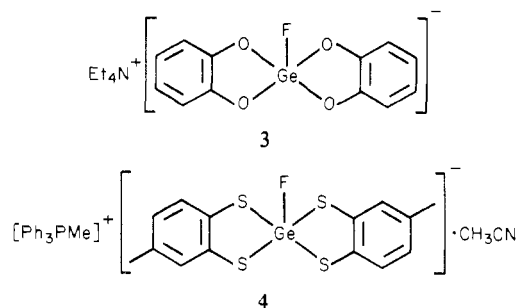

1

2
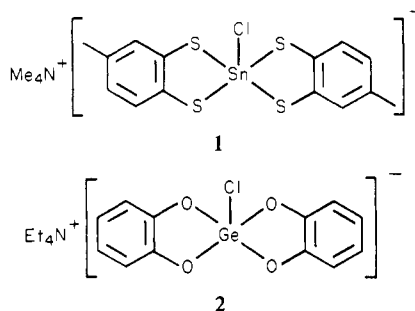
studies on phosphoranes,[9] we found that the rectangular or square-pyramidal geometry may form when a spirocyclic system is present containing unsaturated five-membered rings having like atoms bonded to the central atom in any one ring.

In an extension of our structural studies to related anionic germanium species, we synthesized the first pentacoordinated Ge(IV) compound[10] existing as a square pyramid [(C₆H₄O₂)₂GeCl]⁻Et₄N⁺ (**2**). Previously, pentacoordination for Ge(IV) was confined, primarily, to germatranes containing relatively long Ge–ligand dative bonds.[11] In one case, the crystal structure of an *N*-germylphosphinimine,[12] [Cl₃GeN=PMe₃]₂, revealed a dimeric formulation containing pentacoordinated germanium. For the latter germyl derivative as well as for the germatranes, X-ray analysis showed only the trigonal-bipyramidal geometry.

Since our preliminary report on **2**,[10] we have prepared a range of new anionic pentacoordinated germanium(IV) complexes.[2,13] Reported herein are the crystal structures of two fluoro derivatives, **3** and **4**, containing, respectively, ring oxygen and sulfur atoms. These structures are compared with the chloro derivative **2** and with related main group 4 compounds. The synthesis and characterization of **2**–**4** have been reported.[13]

(1) (a) Pentacoordinated Molecules. 43. (b) Previous paper: Sau, A. C.; Holmes, R. R. *J. Organomet. Chem.* **1981**, *217*, 157.
(2) "Abstracts of Papers", 181st National Meeting of the Americal Chemical Society, Atlanta, GA, March 1981; American Chemical Society: Washington, D.C., 1981; INOR 15.
(3) Sau, A. C.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 3076 and references cited therein.
(4) Aslanov, L. A.; Attiya, V. M.; Ionov, V. M.; Permin, A. B.; Petrosyan, V. S. *J. Struct. Chem.* **1977**, *18*, 844.
(5) Harrison, P. G.; Molloy, K.; Phillips, R. C. *J. Organomet. Chem.* **1978**, *160*, 421.
(6) Einstein, F. W. B.; Penfold, B. R. *Chem. Commun.* **1966**, 780; *J. Chem. Soc. A* **1968**, 3019.
(7) Vergamini, P. J.; Vahrenkamp, H.; Dahl, L. F. *J. Am. Chem. Soc.* **1971**, *93*, 6327.
(8) Sau, A. C.; Day, R. O; Holmes, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 1264.

(9) (a) Holmes, R. R. *Acc. Chem. Res.* **1979**, *12*, 257. (b) Holmes, R. R. "Pentacoordinated Phosphorus. Structure and Spectroscopy". *ACS Monogr.* **1980**, *No. 175*.
(10) Sau, A. C.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 7972.
(11) (a) Bilton, M. S.; Webster, M *J. Chem. Soc., Dalton Trans.* **1972**, 722. (b) Atovmjan, L. O.; Bleidelis, Ja. Ja.; Kemme, A. A.; Shibaeva, R P. *J. Struct. Chem.* **1970**, *11*, 295. (c) Kemme, A. A.; Bleidelis, Ja. Ja.; Shibaeva, R. P.; Atovmjan, L. O. *Ibid.* **1973**, *14*, 90. (d) Dräger, M. *Chem. Ber.* **1975**, *108*, 1723. (e) *Z. Anorg. Allg. Chem.* **1976**, *423*, 53. (f) Gar, T. K.; Khromova, N. Yu.; Gurkova, S. N.; Gusev, A. I.; Mironov, V. F. *Zh. Obshch. Khim.* **1980**, *50*, 1894.
(12) Sheldrick, W. S.; Schomburg, D. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 493.
(13) Sau, A. C.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 4129.

Figure 1. ORTEP plot of the complex $[(C_2H_5)_4N]^+[(C_6H_4O_2)_2GeF]^-$ (3), with thermal ellipsoids at the 50% probability level.

Experimental Section

Space Group Determination and Data Collection for Tetraethylammonium Bis(1,2-benzenediolato)fluorogermanate [(F)Ge-$(C_6H_4O_2)_2]^-Et_4N^+$ (3). A colorless crystal having approximate dimensions of $0.25 \times 0.31 \times 0.37$ mm was cut from a larger crystalline mass and was mounted inside of a sealed thin-walled glass capillary as a precaution against moisture sensitivity. Preliminary investigations using an Enraf-Nonius CAD 4 automated diffractometer and graphite-monochromated molybdenum radiation (fine-focus tube, 45 kV, 20 mA, takeoff angle = 3.1°, $\lambda(K\alpha_1) = 0.709\ 30$ Å, $\lambda(K\alpha_2) = 0.713\ 59$ Å) showed monoclinic $(2/m)$ symmetry. From the observed extinctions $0k0, k = 2n + 1$, and $h0l, l = 2n + 1$, the space group was determined uniquely as $P2_1/c$ $(C_{2h}^5$—No. 14).[14] The lattice constants as determined by the least-squares refinement of the diffraction geometry for 25 reflections having $11.14° \leq \theta_{MoK\alpha} \leq 14.86°$ and measured at an ambient laboratory temperature of 23 ± 2 °C are: $a = 12.886$ (2) Å, $b = 14.870$ (2) Å, $c = 10.912$ (1) Å, and $\beta = 100.29$ (1)°. A unit cell content of four molecules gives a calculated volume of 19.0 Å^3 per nonhydrogen atom, which falls in the range expected for such molecules. The assignment of $Z = 4$ was confirmed by successful solution and refinement of the structure.

Data were collected with the $\theta-2\theta$ scan mode with a θ scan range of $(0.65 + 0.35 \tan \theta)°$ centered about the calculated Mo $K\alpha$ peak position. The scan range was actually extended an extra 25% on either side of the aforementioned limits for the measurement of background radiation. The scan rates varied from 0.59 to 4.0°/min, the rate to be used for each reflection having been determined by a prescan. The intensity, I, for each reflection is then given by $I = (FF/S)(P - 2(B1 + B2))$ where P are the counts accumulated during the peak scan, $B1$ and $B2$ are the left and right background counts, S is an integer which is inversely proportional to the scan rate, and the FF is either unity or a multiplier to account for the occasional attenuation of the diffracted beam. The standard deviation in the intensites, σ_I, was computed as $\sigma_I^2 = (FF/S)^2(P + 4(B1 + B2)) + 0.002I^2$. A total of 3615 independent reflections $(+h,+k,\pm l)$ having $2° \leq 2\theta_{MoK\alpha} \leq 50°$ was measured. Six standard reflections, monitored after every 12 000 s of X-ray exposure time, gave no indication of crystal deterioration or loss of alignment. No corrections were made for absorption ($\mu_{MoK\alpha} = 1.61$ mm^{-1}), and the intensities were reduced to relative amplitudes by means of standard Lorentz and polarization corrections, including corrections for the monochromator.

Solution and Refinement for 3. Initial coordinates for the Ge atom were deduced from a Patterson synthesis, while initial coordinates for the remaining 26 independent nonhydrogen atoms were obtained by standard Fourier difference techniques. Isotropic unit-weighted full-matrix least-squares refinement[15] of the structural parameters for these 27 atoms and a scale factor gave a conventional residual $R = \sum||F_o| - |F_c||/\sum|F_o|$ of 0.093 and a weighted residual $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ of 0.97 for the 1944 reflections having $I \geq 3\sigma_I$ and $(\sin \theta)/\lambda \leq 0.52$. Anisotropic refinement then gave $R = 0.054$ and $R_w = 0.066$. Although the 12 hydrogen atoms of the four methyl groups appeared on a difference Fourier synthesis calculated at this point, many of them were poorly defined and led to geometrically unreasonable bond lengths and angles. Therefore, coordinates for only one hydrogen atom of each of the four methyl groups were taken from the difference synthesis. Coordinates for the
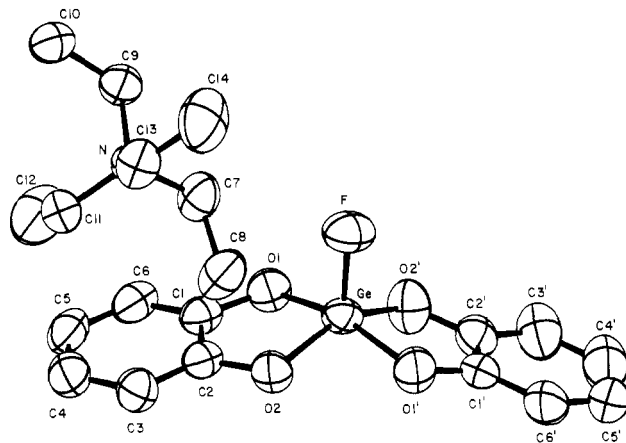
24 remaining indepdent hydrogen atoms were then inferred from the required geometry of the molecule. Since attempts to refine the structural parameters for the hydrogen atoms proved unsuccessful, they were included in all subsequent refinement as fixed isotropic scatterers, having $B = 6.0$ Å^2. The positional parametres for the calculated hydrogen atoms were updated as refinement converged so that their final C–H bond lengths were 0.98 Å.

Variable weighted refinement $(w^{1/2} = 2F_o(Lp)/\sigma_I$, including the 28 independent H atoms as fixed isotropic scatterers, gave $R = 0.032$ and $R_w = 0.043$ for the 2012 reflections having $I \geq 2\sigma_I$ and $(\sin \theta)/\lambda \leq 0.52$. Inclusion of the high-angle data in the refinement led to the final values of $R = 0.035$, $R_w = 0.044$, and GOF[16] = 1.29 for the 2713 independent reflections having $I \geq 2\sigma_I$ and $2° \leq 2\theta_{MoK\alpha} \leq 50°$. During the last cycle of refinement the largest shift in any parameter was 0.02 times its estimated standard deviation. A final Fourier difference synthesis showed a maximum density of 0.306 e/Å^3.

Space Group Determination and Data Collection for the Acetonitrile Monosolvate of Methyltriphenylphosphonium Bis(4-methyl-1,2-benzenedithiolato)fluorogermanate, $[(F)Ge(C_7H_6S_2)_2]^-Ph_3P^+Me\cdot CH_3CN$ (4). Experimental conditions were the same as described for 3, unless otherwise noted. An irregularly shaped, yellow crystal, which can be described as roughly spherical with a diameter of 0.35 mm, was cut from a larger crystalline mass and mounted in a sealed capillary. Preliminary diffractometric investigations showed monoclinic $(2/m)$ symmetry and the extinctions $0k0, k = 2n + 1$, and $h0l, h + l = 2n + 1$, consistent with the uniquely determined space group $P2_1/n$ (alternate setting of $P2_1/c^{14}$). The lattice constants based on 25 reflections having $10.05° \leq \theta_{MoK\alpha} \leq 13.86°$ are $a = 17.108$ (6) Å, $b = 10.566$ (3) Å, $c = 20.630$ (6) Å, and $\beta = 114.01$ (2)°. A unit cell content of four nonsolvated molecules gives a calculated volume of 21.3 Å^3 per nonhydrogen atom. Solution and refinement of the structure disclosed acetonitrile of solvation, leading to the formulation $[(C_7H_6S_2)_2GeF][Ph_3PCH_3]\cdot CH_3CN$, with $Z = 4$.

A total of 5334 independent reflections was measured, monitoring five standard reflections. No corrections were made for absorption $(\mu_{MoK\alpha} = 1.27$ mm^{-1}).

Solution and Refinement for 4. Initial coordinates for the 40 independnet atoms of the nonsolvated species were obtained as described for 3. Isotropic unit-weighted refinement of the structural parameters for these 40 atoms and a scale factor gave $R = 0.132$ and $R_w = 0.155$ for the 2957 reflections having $I \geq 2\sigma_I$ and $(\sin \theta)/\lambda \leq 0.52$. Anisotropic refinement then gave $R = 0.098$ and $R_w = 0.136$. A difference Fourier synthesis at this point showed three independent peaks ($\sim$2.5 e/Å^3), which were interpreted as being the three nonhydrogen atoms of an acetonitrile molecule of solvation. Inclusion of these three atoms in the refinement as isotropic scatterers led to $R = 0.062$ and $R_w = 0.065$. Since attempts to locate the hydrogen atoms of the three methyl groups of the unsolvated molecule on a difference Fourier synthesis proved unsuccessful, they were omitted from the refinement. Coordinates for the 21 independent aromatic hydrogen atoms were calculated, and these were included in subsequent refinement as fixed isotropic scatterers, with $B = 5.0$ Å^2. The positional

(14) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol I, p 99.

(15) The function minimized was $\sum w(|F_o| - |F_c|)^2$. Mean atomic scattering factors were taken from ref 14, 1974; Vol. IV, pp 72–98. Real and imaginary dispersion corrections for Ge, S, F, and O were taken from the same source, pp 149–150.

(16) GOF = $[w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$, where NO = number of observations = 2713 and NV = number of variables = 244.

Table I. Atomic Coordinates in Crystalline [(C$_6$H$_4$O$_2$)$_2$GeF] [NEt$_4$] (3)[a]

atom type[b]	coordinates		
	10^{4}x	10^{4}y	10^{4}z
Ge	2437.8 (3)	466.4 (2)	2155.8 (3)
F	3282 (2)	1267 (2)	1742 (2)
O1	1288 (2)	635 (2)	912 (2)
O1'	3295 (2)	3 (2)	3535 (2)
O2	1704 (2)	1042 (2)	3214 (2)
O2'	2688 (2)	−557 (2)	1334 (2)
N	2410 (2)	4578 (2)	2390 (2)
C1	560 (3)	1176 (2)	1304 (3)
C2	799 (3)	1408 (2)	2574 (3)
C3	117 (3)	1938 (2)	3097 (3)
C4	−804 (3)	2248 (3)	2342 (4)
C5	−1031 (3)	2012 (3)	1098 (4)
C6	−353 (3)	1462 (2)	572 (3)
C1'	3737 (3)	−789 (3)	3253 (4)
C2'	3404 (3)	−1091 (3)	2049 (4)
C3'	3810 (3)	−1871 (3)	1630 (5)
C4'	4539 (4)	−2357 (3)	2450 (7)
C5'	4859 (4)	−2069 (4)	3658 (5)
C6'	4475 (3)	−1263 (4)	4077 (4)
C7	2740 (3)	3601 (3)	2510 (3)
C8	2766 (4)	3182 (3)	3766 (4)
C9	2517 (3)	4871 (3)	1086 (3)
C10	2193 (3)	5842 (3)	771 (4)
C11	1291 (3)	4696 (3)	2601 (4)
C12	463 (4)	4228 (3)	1667 (6)
C13	3086 (3)	5158 (3)	3362 (3)
C14	4240 (4)	5143 (4)	3341 (6)

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

Table II. Fixed Parameters for Hydrogen Atoms in Crystalline [(C$_6$H$_4$O$_2$)$_2$GeF] [NEt$_4$] (3)[a,b]

atom type[c]	coordinates		
	10^{4}x	10^{4}y	10^{4}z
H3	275	2095	3985
H4	−1294	2633	2696
H5	−1680	2236	576
H6	−526	1285	−306
H3'	3587	−2074	765
H4'	4833	−2912	2175
H5'	5363	−2432	4235
H6'	4722	−1043	4926
H71	3449	3555	2309
H72	2244	3256	1903
H91	2075	4476	489
H92	3257	4800	1001
H111	1134	5341	2573
H112	1253	4461	3430
H131	2982	4951	4183
H132	2841	5780	3233
H81	2099	3298	4057
H82	3352	3439	4357
H83	2869	2532	3703
H101	2618	6258	1344
H102	1447	5920	827
H103	2291	5975	−83
H121	595	3581	1698
H122	−235	4349	1878
H123	484	4466	803
H141	4610	5487	4061
H142	4376	5422	2566
H143	4491	4523	3399

[a] See footnote a of Table I. [b] Thermal parameters are fixed at 6.0 Å². [c] Hydrogen atoms are named for the carbon atoms to which they are bonded, where H71 and H72 are bonded to C7, etc.

parameters of these hydrogen atoms were updated as refinement converged so that the final C–H bond lengths were 0.98 Å. No attempt was made to include the hydrogen atoms of the solvent molecule. The

Table III. Atomic Coordinates in Crystalline [(C$_7$H$_6$S$_2$)$_2$GeF] [CH$_3$PPh$_3$]·CH$_3$CN (4)[a]

atom type[b]	coordinates		
	10^{4}x	10^{4}y	10^{4}z
Ge	2143.8 (5)	2221.7 (7)	4845.9 (4)
S1	2701 (1)	2121 (2)	6080 (1)
S2	1510 (2)	4078 (2)	4869 (1)
S1'	1740 (1)	2573 (2)	3631 (1)
S2'	3446 (1)	1593 (2)	4951 (1)
P	5170 (1)	4423 (2)	2980 (1)
F	1446 (3)	907 (4)	4717 (2)
C1	2110 (4)	3299 (6)	6267 (4)
C2	1574 (4)	4137 (6)	5743 (4)
C3	1115 (5)	5050 (7)	5926 (4)
C4	1183 (4)	5210 (7)	6612 (4)
C5	1718 (5)	4390 (8)	7113 (4)
C6	2151 (4)	3439 (7)	6952 (4)
C7	694 (5)	6281 (8)	6799 (5)
C1'	2560 (4)	1759 (6)	3501 (3)
C2'	3288 (4)	1311 (6)	4072 (3)
C3'	3892 (4)	628 (6)	3939 (4)
C4'	3825 (5)	373 (7)	3249 (4)
C5'	3113 (5)	861 (8)	2694 (4)
C6'	2503 (4)	1530 (8)	2819 (4)
C7'	4509 (5)	−427 (8)	3132 (5)
CA1	4453 (4)	3511 (6)	2243 (3)
CA2	3644 (5)	3977 (7)	1824 (4)
CA3	3115 (5)	3325 (8)	1241 (4)
CA4	3369 (5)	2209 (7)	1062 (4)
CA5	4167 (5)	1717 (7)	1476 (4)
CA6	4707 (4)	2368 (6)	2063 (4)
CB1	4647 (4)	4984 (6)	3509 (3)
CB2	3954 (4)	4339 (7)	3537 (4)
CB3	3590 (4)	4780 (7)	3992 (4)
CB4	3902 (5)	5834 (8)	4399 (4)
CB5	4579 (5)	6464 (7)	4364 (4)
CB6	4952 (4)	6067 (7)	3928 (4)
CC1	6033 (4)	3409 (6)	3502 (3)
CC2	5868 (5)	2502 (7)	3919 (4)
CC3	6489 (5)	1606 (7)	4273 (4)
CC4	7261 (5)	1636 (7)	4224 (4)
CC5	7425 (5)	2544 (8)	3824 (5)
CC6	6824 (4)	3441 (7)	3465 (4)
CM	5548 (5)	5774 (6)	2648 (4)
CN1	5049 (8)	3385 (13)	407 (7)
CN2	5543 (9)	4249 (17)	890 (7)
N	6012 (7)	5178 (17)	1286 (7)

[a] See footnote a of Table I. [b] Atoms are labeled to agree with Figure 2.

final cycles of refinement (43 nonhydrogen atoms anisotropic, 21 hydrogen atoms fixed isotropic) employing variable weights and including the high-angle data led to $R = 0.058$, $R_w = 0.073$, and $S = 1.878$[17] for the 3579 reflections having $I \geq 2\sigma_I$ and $2° \leq 2\theta_{Mo K\alpha} \leq 50°$. During the final cycle of refinement, the largest Δ/σ was 0.02. The only density of any consequence on a final difference Fourier synthesis was in the immediate vicinity of the Ge atom.

Computations were done on a CDC Cyber-175 computer using LINEX, a modification of the Busing and Levy full-matrix least-squares program ORFLS, Johnson's thermal ellipsoid plot program ORTEP, the Oak Ridge Fortran function and error program ORFFE, Zalkin's Fourier program FORDAP, and several locally written programs.

Results and Discussion

The atom labeling schemes for **3** and **4** are shown in the ORTEP plots of Figures 1 and 2, respectively. Both anions have a pseudo-2-fold axis coincident with the Ge–F bond. To facilitate the examination of this pseudosymmetry, the atoms of the anions are named so that the primed atoms go into the unprimed ones by the pseudo-2-fold axis.

Atomic coordinates for **3** are given in Tables I and II, and atomic coordinates for **4** are given in Tables III and IV. Bond lengths and angles for **3** are given in Table V, and these pa-

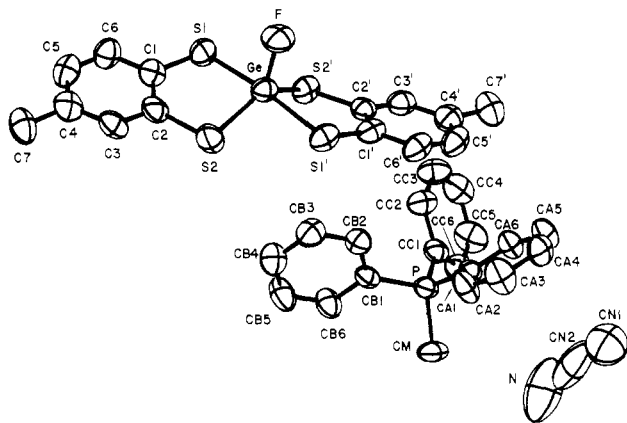(17) As defined in footnote 16, but with NO = 3579 and NV = 388.

Figure 2. ORTEP plot of the complex [CH₃PPh₃]⁺-[(C₇H₆S₂)₂GeF]⁻·CH₃CN (**4**), with thermal ellipsoids at the 50% probability level.

Table IV. Fixed Parameters for Hydrogen Atoms in Crystalline [(C₇H₆S₂)₂GeF] [CH₃PPh₃]·CH₃CN (4)[a]

atom type[b]	coordinates		
	$10^4 x$	$10^4 y$	$10^4 z$
H3	726	5606	5553
H5	1790	4489	7607
H6	2498	2847	7324
H3'	4392	306	4342
H5'	3046	726	2204
H6'	2008	1858	2414
HA2	3454	4780	1949
HA3	2547	3664	948
HA4	2986	1751	638
HA5	4347	905	1350
HA6	5274	2023	2356
HB2	3723	3586	3244
HB3	3104	4326	4017
HB4	3641	6135	4715
HB5	4082	7218	4658
HB6	5434	6541	3908
HC2	5318	2946	3962
HC3	6373	950	4559
HC4	7698	1003	4476
HC5	7983	2555	3794
HC6	6951	4096	3184

[a] See footnote *a* of Table I. [b] Hydrogen atoms are named for the carbon atoms to which they are bonded.

rameters for the anion in **4** are given in Table VI. Bond lengths and angles for the cation and solvent moieties in **4** and thermal parameters for both **3** and **4** are provided as supplementary material.

As can be seen in the plots of Figures 1 and 2, the molecular geometry about the Ge atom in **3** is closer to the idealized rectangular pyramid (RP), while for **4** this geometry is closer to that of the idealized trigonal bipyramid (TP). Both geometries lie on the Berry coordinate[18] connecting the TP (ligand atoms 1 and 1' axially placed, 2 and 2' equatorial) to the RP (F apical) where F is the pivotal atom. In terms of this coordinate,[9,19] **3** is displaced 82.5% (80.6% with use of unit vectors) from the TP toward the RP, while **4** is displaced only 47.5% (40.3% with use of unit vectors).

For **3**, the dihedral angle between the least-squares mean plane defined by the atoms Ge, F, O1, and O1' (plane I; Table VII) and the one defined by Ge, F, O2, and O2' (plane II; Table VII) is 89.7°. For **4**, the corresponding dihedral angle is 88.3° (planes IV and V; Table VII). These angles are both in the range expected[20] for geometries which conform to the

(18) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.
(19) Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318.

Table V. Bond Lengths (Å) and Bond Angles (Deg) for [(C₆H₄O₂)₂GeF] [NEt₄] (3)[a]

Ge–O1	1.839 (2)	C1'–C2'	1.382 (5)
Ge–O1'	1.835 (2)	C2'–C3'	1.383 (5)
Ge–O2	1.831 (2)	C3'–C4'	1.379 (7)
Ge–O2'	1.825 (2)	C4'–C5'	1.378 (7)
Ge–F	1.727 (2)	C5'–C6'	1.404 (7)
O1–C1	1.361 (4)	C6'–C1'	1.380 (5)
O1'–C1'	1.367 (5)	N–C7	1.513 (4)
O2–C2	1.361 (4)	N–C9	1.517 (4)
O2'–C2'	1.354 (4)	N–C11	1.510 (4)
C1–C2	1.407 (4)	N–C13	1.515 (5)
C2–C3	1.378 (5)	C7–C8	1.501 (5)
C3–C4	1.396 (5)	C9–C10	1.526 (5)
C4–C5	1.382 (6)	C11–C12	1.507 (6)
C5–C6	1.394 (5)	C13–C14	1.491 (6)
C6–C1	1.367 (5)		
O1–Ge–O1'	160.8 (1)	C6–C1–C2	120.8 (3)
O2–Ge–O2'	149.0 (1)	C1–C2–C3	120.3 (3)
O1–Ge–O2	87.9 (1)	C2–C3–C4	118.8 (3)
O1'–Ge–O2'	87.5 (1)	C3–C4–C5	120.3 (4)
O1–Ge–O2'	86.6 (1)	C4–C5–C6	121.0 (3)
O1'–Ge–O2	87.8 (1)	C5–C6–C1	118.7 (3)
F–Ge–O1	100.1 (1)	C6'–C1'–C2'	121.0 (4)
F–Ge–O1'	99.1 (1)	C1'–C2'–C3'	121.0 (4)
F–Ge–O2	105.2 (1)	C2'–C3'–C4'	118.6 (5)
F–Ge–O2'	105.8 (1)	C3'–C4'–C5'	120.7 (5)
Ge–O1–C1	111.0 (2)	C4'–C5'–C6'	120.9 (4)
Ge–O1'–C1'	110.6 (2)	C5'–C6'–C1'	117.8 (5)
Ge–O2–C2	110.8 (2)	C7–N–C9	106.6 (3)
Ge–O2'–C2'	111.6 (2)	C7–N–C11	111.0 (3)
O1–C1–C2	114.4 (3)	C7–N–C13	111.6 (3)
O1'–C1'–C2'	115.0 (3)	C9–N–C11	111.0 (3)
O2–C2–C1	115.1 (3)	C9–N–C13	110.9 (3)
O2'–C2'–C1'	114.9 (3)	C11–N–C13	105.8 (3)
O2–C2–C3	124.6 (3)	N–C7–C8	116.0 (3)
O2'–C2'–C3'	124.1 (4)	N–C9–C10	114.6 (3)
O1–C1–C6	124.7 (3)	N–C11–C12	115.0 (4)
O1'–C1'–C6'	124.0 (4)	N–C13–C14	115.6 (4)

[a] See footnotes *a* and *b* of Table I.

Table VI. Bond Lengths (Å) and Bond Angles (Deg) for [(C₇H₆S₂)₂GeF]⁻[CH₃PPh₃]⁺·CH₃CN (4)[a]

Ge–F	1.780 (4)	C4–C5	1.374 (10)
Ge–S1	2.330 (2)	C5–C6	1.368 (10)
Ge–S1'	2.343 (2)	C6–C1	1.392 (9)
Ge–S2	2.251 (2)	C4–C7	1.547 (10)
Ge–S2'	2.250 (2)	C1'–C2'	1.404 (8)
S1–C1	1.744 (7)	C2'–C3'	1.376 (9)
S1'–C1'	1.756 (7)	C3'–C4'	1.405 (9)
S2–C2	1.761 (7)	C4'–C5'	1.388 (10)
S2'–C2'	1.746 (6)	C5'–C6'	1.369 (10)
C1–C2	1.410 (1)	C6'–C1'	1.390 (9)
C2–C3	1.391 (9)	C4'–C7'	1.541 (10)
C3–C4	1.381 (9)		
F–Ge–S1	94.5 (2)	S2'–C2'–C3'	119.1 (5)
F–Ge–S1'	94.4 (2)	S2–C2–C1	120.9 (6)
F–Ge–S2	112.6 (2)	S2'–C2'–C1'	121.5 (5)
F–Ge–S2'	111.2 (2)	C1–C2–C3	119.3 (7)
S1–Ge–S2	90.16 (7)	C1'–C2'–C3'	119.4 (6)
S1'–Ge–S2'	89.92 (7)	C2–C3–C4	122.8 (7)
S2–Ge–S1'	87.13 (7)	C2'–C3'–C4'	122.9 (7)
S2–Ge–S2'	136.22 (9)	C3–C4–C5	116.5 (7)
S1–Ge–S2'	86.13 (7)	C3'–C4'–C5'	116.6 (7)
S1–Ge–S1'	171.06 (7)	C4–C5–C6	122.8 (7)
Ge–S1–C1	101.1 (2)	C4'–C5'–C6'	121.0 (7)
Ge–S1'–C1'	100.4 (2)	C5–C6–C1	121.0 (7)
Ge–S2–C2	102.9 (2)	C5'–C6'–C1'	122.4 (7)
Ge–S2'–C2'	102.8 (2)	C6–C1–C2	117.5 (7)
S1–C1–C2	122.2 (5)	C6'–C1'–C2'	117.6 (7)
S1'–C1'–C2'	121.9 (5)	C7–C4–C3	121.1 (7)
S1–C1–C6	120.4 (6)	C7'–C4'–C3'	120.6 (7)
S1'–C1'–C6'	120.5 (5)	C7–C4–C5	122.4 (7)
S2–C2–C3	119.8 (6)	C7'–C4'–C5'	122.8 (7)

[a] See footnotes *a* and *b* of Table III.

Table VII. Deviations (A) from Some Least-Squares Mean Planes[a]

| | [Et₄N]⁺[(C₆H₄O₂)₂GeF]⁻ (3) | | | [MePPh₃]⁺[(C₇H₆S₂)₂GeF]⁻·CH₃CN (4) | |
	I[d]	II	III	IV[d]	V
Ge[b]	0.007	0.002	(-0.398)	Ge[c]	-0.010	-0.003
F	-0.001	-0.000	(-2.124)	F	-0.001	0.001
O1	-0.003	(-1.809)	-0.118	S1	0.011	(2.317)
O1'	-0.003	(1.813)	0.110	S1'	0.000	(-2.339)
O2	(1.776)	-0.001	-0.064	S2	(-2.092)	0.001
O2'	(-1.746)	-0.001	0.072	S2'	(2.082)	0.001

[a] Entries in parentheses are for atoms not included in the calculation of the plane. [b] Atoms are labeled to agree with Figure 1. [c] Atoms are labeled to agree with Figure 2. [d] Dihedral angles: I and II = 89.7°; IV and V = 88.3°.
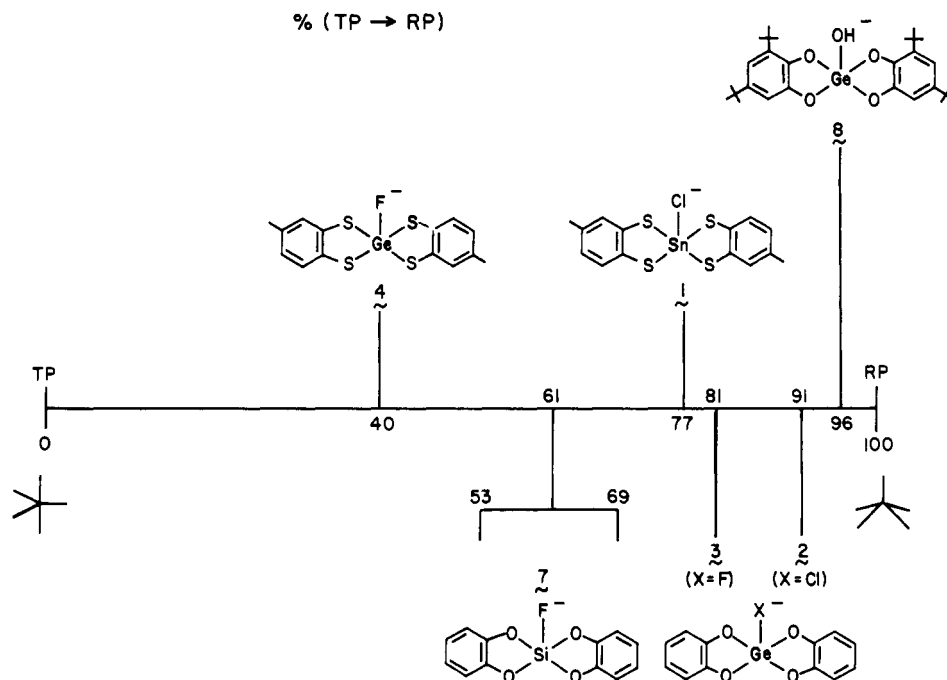

Figure 3. Structural displacement along the C_{2v} Berry coordinate connecting the idealized trigonal bipyramid and rectangular pyramid (% TP → RP) for anionic pentacoordinated main-group 4 spirocyclic complexes. Structure **8** is given in ref 25. With reference to the central atom, the structural displacement toward the RP increases in the order Si < Ge < Sn.

C_{2v} constraint of the Berry coordinate. For **3**, the atoms forming the basal plane of the RP (O1, O1', O2, and O2') are coplanar to within ±0.1 Å (plane III; Table VII), with the Ge atom displaced 0.4 Å out of this plane in a direction toward the apical F atom.

Concomitant with residual TP character for **4**, the bonds from Ge to the axial ligand atoms are, on the average, 0.09 Å larger than the bonds to the equatorial ligand atoms. For **3**, where less residual TP character would be expected, this difference is only 0.01 Å.

The Ge–F bond length in **4** (1.780 (4) Å) is significantly longer than the Ge–F bond length in **3** (1.727 (2) Å). As found with cyclic phosphoranes,[9,21] the unique apical bond becomes shorter, in general, as the pentacoordinated structure more closely approaches the rectangular pyramid. This bond length change is in accord with the VSEPR theory as previously discussed.[22] VSEPR theory[23] suggests that the presence of the more electronegative ring oxygen atoms in **3** should result in a reduced bond electron-pair-repulsion effect between the ring bonds and the unique bond compared to that in the thio derivative **4**. This effect could stabilize the inherently higher energy rectangular pyramid relative to the trigonal

bipyramid.[9,23] The presence of larger sulfur atoms also may contribute to a lengthening of the Ge–F bond length.

Additional structural effects attributable to electronegativity and size changes are seen in Figure 3. These structures fall on the Berry exchange coordinate connecting the trigonal bipyramid and rectangular pyramid.[8,10,24,25] The extent to which the latter structure is approached increases as one descends the periodic table for group 4 central atoms. This agrees with lessened electron-pair-repulsion effects associated with the ligand bonds connected to the larger and presumably less electronegative central atom.[9] As above, this effect stabilizes the normally higher energy rectangular pyramid. Thus, Figure 3 shows the X-ray structure of the anionic fluoro germanate **3** more displaced toward the rectangular pyramid than that of the related fluorosilicate[24] analogue **7**. Similarly, of the spiro dithia derivatives, the structure of the anionic tin compound[8] **1** is displaced more toward the rectangular pyramid than the germanium complex **4**. Although the comparison is between the chloro and fluoro derivatives in the latter instance, it is felt that the change in central atom acts as the most important factor in accounting for the structural displacement between the two pentacoordinate complexes. This reasoning stems largely from the small structural change seen between the fluoro and chloro germanium derivatives **3** and **2**[10] and an

(20) Brown, R. K.; Holmes, R. R. *J. Am. Chem. Soc.* **1977**, *99*, 3326.
(21) Holmes, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 5379.
(22) Holmes, R. R. *J. Am. Chem. Soc.* **1974**, *96*, 4143.
(23) (a) Gillespie, R. J. *Inorg. Chem.* **1966**, *5*, 1634. (b) Gillespie, R. J. "Molecular Geometry"; Van Nostrand-Reinhold: New York, 1972, and references cited therein.

(24) Harland, J. J.; Day, R. O.; Vollano, J. F.; Sau, A. C.; Holmes, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 5269.
(25) Day, R. O.; Holmes, R. R., unpublished data.

even smaller change between the isoelectronic fluoro[26] and chloro[27] phosphoranes **5** and **6**. The latter structures are displaced 65% (F) and 72% (Cl) based on the dihedral angle method[9,19] using actual bond distances.

5, X = F
6, X = Cl
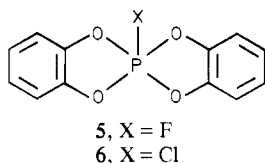
For the fluorosilicate **7**, it is evident that crystal packing[24] also is of some importance. As we have shown by taking proper cognizance of intermolecular effects, e.g., those due to steric terms[28] or hydrogen bonding,[29] structural changes due to substituent effects may be reliably ascertained. In view of these studies, and the absence of large intermolecular steric effects indicated for the structures compared here, **1–7**, it is felt that the substituent effects mentioned are the main factors responsible for structural placement in this series.

Thus far, the pentacoordinate stereochemistry for main group 4 elements displays a marked similarity to that for

phosphoranes[9,19] and follows the general structural principles developed for phosphoranes. It seems reasonable that nonrigid behavior typified by intramolecular ligand exchange should be found for some anionic pentacoordinated members of group 4[30] like that observed for phosphoranes[9] and that reaction mechanisms of group 4 compounds based on pentacoordinate transition states should follow the general features developed for mechanisms postulated for related phosphorus reactions.[31]

Registry No. 3, 76375-58-1; **4,** 79769-92-9.

Supplementary Material Available: Anisotropic thermal parameters (Tables A and B, respectively, for **3** and **4**), bond lengths and angles for the MePPh$_3^+$ cation and acetonitrile solvent for **4** (Table C), and a listing of observed and calculated structure factor amplitudes for **3** and **4** (27 pages). Ordering information is given on any current masthead page.

(26) Wunderlich, H.; Mootz, D. *Acta. Crystallogr., Sect. B* **1974,** *30,* 935.
(27) Brown, R. K.; Holmes, R. R. *Inorg. Chem.* **1977,** *16,* 2294.
(28) Brown, R. K.; Day, R. O.; Husebye, S.; Holmes, R. R. *Inorg. Chem.* **1978,** *17,* 3276.
(29) Meunier, P. F.; Deiters, J. A.; Holmes, R. R. *Inorg. Chem.* **1976,** *15,* 2572.
(30) For some tin(IV) cyclic derivatives rendered pentacoordinated by formation of intramolecular Sn←N dative bonding, NMR data provide evidence for the possibility of ligand exchange occurring by a Berry pseudorotation process. See: Van Koten, G.; Noltes, J. G. In "Organotin Compounds: New Chemistry and Applications"; Zuckerman, J. J., Ed. *Adv. Chem. Ser.* **1976,** *No. 157,* 275. Zschunke, A.; Tzschuch, A.; Pönicke, K. *J. Organomet. Chem.* **1973,** *51,* 197.
(31) Holmes, R. R. "Pentacoordinated Phosphorus. Reaction Mechanisms". *ACS Monogr.* **1980,** *No. 176.*

Contribution from the Department of Chemistry and Molecular Structure Center,
Indiana University, Bloomington, Indiana 47405

Bis(dimethylamine)tetrakis(*tert*-butyl mercaptido)di-μ-sulfido-dimolybdenum(IV)

M. H. CHISHOLM,* J. F. CORNING, and J. C. HUFFMAN

Mo$_2$(NMe$_2$)$_6$ (M≡M) reacts with *t*-BuSH (≥6 equiv) in hydrocarbon solvents at room temperature to give the green crystalline compound Mo$_2$(μ-S)$_2$(*t*-BuS)$_4$(HNMe$_2$)$_2$, which has been characterized by a single-crystal X-ray diffraction study. Each molybdenum atom is in a distorted trigonal-bipyramidal environment with respect to the atoms to which it is directly bonded. The halves of the molecule are joined together by a pair of sulfido bridges, which form alternately long (axial), 2.327 (1) Å, and short (equatorial), 2.238 (1) Å, bonds. The Mo–Mo distance is 2.730 (1) Å, indicative of M–M bonding, which, in a formal sense, may be viewed as a double bond, $\sigma^2\pi^2$. The *tert*-butyl mercaptido groups occupy equatorial sites (Mo–S = 2.325 (2) Å), and the dimethylamino ligands, the remaining axial positions (Mo–N = 2.368 (2) Å). These results are compared with related molybdenum compounds. Crystal data for Mo$_2$(μ-S)$_2$(*t*-BuS)$_4$(HNMe$_2$)$_2$: space group *A2/m*, *a* = 11.392 (2) Å, *b* = 17.291 (3) Å, *c* = 9.304 (1) Å, and *β* = 103.96 (1)°.

Introduction

The reactions between Mo$_2$(NMe$_2$)$_6$ and alcohols give dinuclear alkoxides Mo$_2$(OR)$_6$ with retention of the molybdenum–molybdenum triple bond when the alkyl group is bulky, e.g., R = *t*-Bu, *i*-Pr, and CH$_2$CMe$_3$.[1] With less bulky alkoxy ligands such as EtO and MeO, polymeric and as yet not well-characterized compounds of empirical formula Mo(OR)$_3$ are formed.[1] As part of a general program aimed at elucidating the coordination chemistry of the (Mo≡Mo)$^{6+}$ unit,[2,3] we investigated the reactions between Mo$_2$(NMe$_2$)$_6$ and bulky

thiols RSH (R = *t*-Bu, *i*-Pr, and CH$_2$Ph). We herein report our findings of these studies.

Results and Discussion

Syntheses. Hydrocarbon solutions of Mo$_2$(NMe$_2$)$_6$ react readily with the thiols RSH, where R = *t*-Bu, *i*-Pr, and CH$_2$Ph (≥6 equiv), at room temperature to produce very sparingly soluble precipitates. Reactions involving *t*-BuSH yielded dark green crystals of the title compound in close to quantitative yields based on molybdenum. The reactions involving *i*-PrSH and PhCH$_2$SH yielded finely divided, microcrystalline products, which were not suitable for single-crystal X-ray studies.

The new compounds are air sensitive and readily hydrolyzed in the atmosphere. They are thermally unstable above 60 °C in vacuo and cannot be sublimed. They are very sparingly soluble in benzene and toluene, barely soluble enough to allow

(1) Chisholm, M. H.; Cotton, F. A.; Murillo, C. A.; Reichert, W. W. *Inorg. Chem.* **1977,** *16,* 1801.
(2) Chisholm, M. H.; Cotton, F. A. *Acc. Chem. Res.* **1978,** *11,* 356.
(3) Chisholm, M. H. *Symp. Faraday Soc.* **1980,** *14,* 194.