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The Crystal Structures of 2,2′-Bipyridyltetrafluorosilicon(IV), 2,2′-Bipyridyltetrafluorogermanium(IV), and 2,2′-Bipyridyltetrafluorotin(IV)

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Received August 3, 1971

The molecular structures of 2,2′-bipyridyltetrafluorosilicon(IV), $SiF_4C_{10}H_8N_2$, 2,2′-bipyridyltetrafluorogermanium(IV), $GeF_4C_{10}H_8N_2$, and 2,2′-bipyridyltetrafluorotin(IV), $SnF_4C_{10}H_8N_2$, have been determined by single-crystal X-ray diffraction. The compounds were crystallized from nitromethane, and in the case of the germanium and tin complexes, two modifications of each were obtained: an unsolvated form and a monosolvated form, unstable to loss of solvent on air-drying. The unit cell constants are as follows: for $SiF_4C_{10}H_8N_2$, space group $P2_1/c$ (no. 14), $Z = 4$, $a = 7.195$ (2), $b = 9.185$ (2), $c = 16.821$ (5) Å, $\beta = 106.85$ (2)°; for $GeF_4C_{10}H_8N_2 \cdot CH_3NO_2$, space group $P2_1/m$ (no. 11), $Z = 2$, $a = 11.958$ (3), $b = 6.924$ (2), $c = 8.317$ (2) Å, $\beta = 96.16$ (2)°; for $SnF_4C_{10}H_8N_2 \cdot CH_3NO_2$, space group $P2_1/c$ (no. 14), $Z = 4$, $a = 8.844$ (2), $b = 11.646$ (4), $c = 13.420$ (5) Å, $\beta = 94.04$ (2)°. The stable forms of the germanium and tin complexes are possibly disordered, either in space group $P6_2$ (no. 171) or space group $P6_4$ (no. 172), where $a = 11.631$ (3), $b = 20.319$ (5) Å and $a = 12.06$ (3), $b = 20.56$ (5) Å, respectively; the crystal structures remain unsolved. All three compounds are monomeric, the solvent is not coordinated, and the coordination is the expected distorted cis octahedral.

Introduction

Considerable efforts in the study of six-coordinate adducts of the elements of group IVa have not been very extensively supported by crystal structure analyses.[1-9] This is due partly to the reactivity of the compounds and to the difficulty in obtaining suitable crystals and partly to the fact that the main structural question, that of cis–trans isomerism, may sometimes be settled by infrared or nmr techniques. Preference of group IVa tetrahalide adducts for cis or trans configurations has been quite extensively discussed in terms of p_π–d_π bonding effects and steric effects.[10-14] It was hoped that trends observed in these structures might indicate the magnitude of these effects. The three compounds described here are remarkably insensitive to moisture and are rather insoluble in nonpolar or moderately polar solvents. The crystal structure determinations were undertaken to determine whether the compounds are monomeric, like bis(pyridine)tetrafluorosilicon(IV) $(SiF_4(C_5H_5N)_2$,[3] or polymeric, like the complex of tin tetrachloride with glutaronitrile $(SnCl_4$-$NC(CH_2)_3CN)$.[8] We also hoped to detect a structural trans effect similar to that reported for tripyridyltrichlorothallium(III).[15]

Experimental Section

Samples of $SiF_4C_{10}H_8N_2$, $GeF_4C_{10}H_8N_2$, and $SnF_4C_{10}H_8N_2$ were prepared as previously described.[12,16-18] The solvents chloroacetonitrile, nitromethane, and *N,N*-dimethylformamide were found to dissolve the complexes appreciably without decomposition, and crystals were grown easily by cooling warm saturated solutions. The silicon complex crystallized from all three solvents as well-formed parallelepipeds. Crystals of the other two compounds appeared to be of two types when grown from nitromethane or chloroacetonitrile: an unstable form which, when removed from the solution and allowed to dry, crumbled to form masses of tiny crystals apparently identical with the second, stable form, which had the external appearance of hexagonal bipyramids. From solutions in *N,N*-dimethylformamide, only the stable crystalline modifications were produced.

Unit Cell Determination

Monochromatic Mo Kα radiation (λ 0.71069 Å) was obtained by Bragg reflection of the direct beam (takeoff angle 2.0°) from the (002) planes of a highly oriented graphite "crystal." The planes in which diffraction occurs at the monochromator and sample crystal were perpendicular. An incident beam collimator with a 0.5-mm diameter pinhole situated 140 mm from the monochromator crystal was used, together with a diffracted beam-receiving aperture 4 mm square, 230 mm from the crystal, and 20 mm in front of a scintillation counter. Accurate values of the four angles 2θ, ω, χ, and ϕ were obtained for 12 Bragg reflections from the specimen crystal, widely separated in the reciprocal lattice and at as high a value of 2θ as compatible with obtaining reasonable intensity (*ca.* 500 cps). The method used involved systematic missetting of 2θ, ω, and χ until the intensity of diffraction was diminished by half, under automatic control by a PDP 8/S computer using the alignment program supplied by the Picker-Nuclear Co. This centering process was repeated in the negative range of 2θ for all 12 reflections and the values of 2θ, ω, and χ were appropriately averaged. The unit cell constants given below result from least-squares refinement of approximate values obtained from photographs, together with approximate angles for two reference reflections, against the 12 observed sets of diffraction angles.

Data Collection and Reduction

For data collection, the incident beam collimator pinhole was increased to 1-mm diameter, and the takeoff angle, to 3.0°; all other parameters were unchanged. A pulse height analyzer, used in combination with the scintillation counter, was set to receive 100% of the Mo Kα peak. The θ–2θ scanning technique was used with a base width at low 2θ dependent on the mosaicity of the crystal under study and increasing with 2θ to allow for α_1–α_2 dispersion. A 2θ scan speed of 1°/min was used. Attenuators made of multiple nickel foils were inserted automatically in order to limit the counting rate to less than 10^4 cps. In-

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strumental and crystal stabilities were checked by monitoring a single reference reflection every 30 measurement cycles and also measuring the intensities of all diffractions on the three reciprocal axes for positive and negative indices before and after data collection. No untoward variations were observed with any of the crystals.

Data reduction was performed using a locally written program for the CDC 3300 computer. This program also determined an approximate scale factor and overall thermal parameter from reflection statistics.[19] The reflection intensity I was computed as $[N - (B_1 + B_2)t_s/2t_b]$ and the standard deviation $\sigma(I) = [N + (B_1 + B_2)(t_s/2t_b)^2 + (0.02N)^2]^{1/2}$, where N and B are the counts accumulated during the scan time t_s and background time t_b, respectively. All data for which $I < 3\sigma(I)$ were rejected (used in neither structure solution nor refinement) and the data remaining were corrected for Lorentz and polarization effects, $(Lp)^{-1} = \sin 2\theta_s(\cos^2 2\theta_m + 1)/(\cos^2 2\theta_m + \cos^2 2\theta_s)$, where $2\theta_s$ and $2\theta_m$ are the diffraction angles at the sample crystal and monochromator, respectively. Absorption corrections[20,21] (*vide infra*) were applied in the case of the germanium and tin compounds after structure solutions and isotropic refinement.

Structure Solution and Refinement

The Sir George Williams University CDC 3300 computer was used throughout for crystallographic computing. In least-squares procedures[22] the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $w = [\sigma(F_o)]^{-2}$ and the discrepancy indices referred to are $R = [\Sigma(||F_o| - |F_c||)/\Sigma|F_o|]$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. The "goodness of fit" parameter is $[\Sigma w(|F_o| - |F_c|)^2/(n - m)]^{1/2}$ where n and m are numbers of observations and variables, respectively. Scattering factors for neutral oxygen, nitrogen, carbon, and hydrogen were taken from the compilation of Ibers,[23a] and those for silicon, germanium, and tin were the Thomas–Fermi–Dirac values.[23b] In the latter (anisotropic) stages of refinement the scattering factors for germanium and tin were corrected for anomalous dispersion.[23c] The anisotropic thermal parameters used took the form $\exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + 2hkb_{12} + 2hlb_{13} + 2klb_{23})]$.

$SiF_4C_{10}H_8N_2$.—A preliminary photographic survey of Weissenberg $0kl$, $1kl$, and precession $h0l$, $h1l$, $hk0$ zones uniquely established the space group as $P2_1/c$ (no. 14) and testified to the suitable quality of the crystal chosen for diffractometry (a parallelepiped *ca.* 0.5 × 0.2 × 0.2 mm). The unit cell parameters a = 7.195 (2), b = 9.185 (2), c = 16.821 (5) Å, β = 106.85 (2)°, and V = 1063.9 Å^3 at 24 (1)° were obtained, as described above, after transferring the crystal to a Picker automated four-circle diffractometer. The observed density obtained by flotation in an iodoethane–benzene mixture was 1.63 (2) g cm^{-3}, while that calculated for Z = 4 and M = 260.27 amu is 1.624 g cm^{-3}.

An asymmetric set of 1398 diffraction intensities was collected in the range 4° < 2θ < 45°, there being no significantly intense reflections above 2θ = 45°, while the backstop intervened below 4°. The base scan range used was 1.5°, safely encompassing the diffraction peaks (approximately 0.7° wide at low 2θ values). Photographs taken with a film placed just in front of the counter showed no vignetting of the diffracted beam by the receiving collimator or slits. After data reduction 1120 reflections remained.

Inspection of a sharpened three-dimensional Patterson synthesis[24,25] suggested several possible positions for the silicon atom and two axial fluorine atoms each of which were tested in trial structure factor calculations. Assuming the positions which had resulted in the best fit to be essentially correct (R = 57.5%), further interpretation of the Patterson synthesis yielded likely positions for the other two fluorine atoms and the two nitrogen atoms. A three-dimensional Fourier synthesis phased by these five atoms (R = 49.8%) provided the unambiguous location of all the carbon atoms and confirmed the assignment of the starting set. Four cycles of full-matrix least-squares refinement of individual positional and isotropic thermal parameters led to convergence at R = 13.1% and R_w = 8.9%. A three-dimensional difference Fourier synthesis calculated following the last cycle of refinement showed peaks varying from 0.5 to 0.8 e/Å^3 at positions where hydrogen atoms were expected and some residual asymmetric electron density about the other atom positions but no other significant features. Refinement was continued using individual anisotropic thermal parameters. The hydrogen atoms in computed positions were included in the structure factor calculations but not the refinement. During this phase of the refinement, computer memory restrictions necessitated dividing the parameters into two matrices; the scale factor and parameters for silicon and fluorine atoms were placed in the first matrix and the other parameters were divided equally between the matrices. After each cycle the nitrogen and carbon atom parameters were randomly shuffled between matrices in an attempt to maintain some interaction between all parameters. After seven cycles of refinement all shifts in parameters were less than $^1/_{20}$ of their standard deviations, R = 5.6%, R_w = 6.9%, and the "goodness of fit" parameter was 1.75. The final atomic parameters are shown in Table IA.[26]

$GeF_4C_{10}H_8N_2$ and $SnF_4C_{10}H_8N_2$, Stable Forms.—The crystals of these compounds which were stable when dry were shown by Weissenberg $hk0$, $hk1$, $hk2$ and precession $h0l$, $0kl$ zones to be isomorphous. The Laue symmetry, coupled with the systematic absence of all $00l$ with $l \neq 3n$, implied space group $P6_2$ (no. 171) or $P6_4$ (no. 172). (Only minor differences in a few observed reflections indicated the Laue group $6/m$ rather than $6/mmm$.) The unit cell constants are as follows: for $GeF_4C_{10}H_8N_2$, a = 11.631 (3), c = 20.319 (5) Å, V = 2380.5 Å^3 measured as described above on the diffractometer; for $SnF_4C_{10}H_8N_2$, a = 12.06 (3), c = 20.56 (5) Å, V = 2589.7 Å^3 measured from uncalibrated precession photographs. The observed density of 1.90 g cm^{-3} for the germanium compound, measured by flotation in an iodoethane–benzene mixture, requires ≃9 molecules per unit cell assuming no solvation. (No solvent was lost on heating the crystals to 150°.) Diffractometer data were collected for the germanium complex and a three-dimensional Patterson synthesis was computed; no solution consistent with all strong peaks could be found. Thus it was felt that the crystals were possibly disordered, and at this stage, investigation of this modification of both compounds was deferred.

$GeF_4C_{10}H_8N_2 \cdot CH_3NO_2$.—A crystal of the unstable form of the germanium complex was transferred rapidly to a capillary, the inside surface of which had been previously wetted with the mother liquor. The capillary was sealed with a small flame. The selected crystal was a rectangular plate *ca.* 0.38 × 0.30 × 0.20 mm. Interpretation of Weissenberg $0kl$, $1kl$, and precession $h0l$, $h1l$, $hk0$, $hk1$ photographs limited the space group assignment to $P2_1/m$ (no. 11) or $P2_1$ (no. 4). The unit cell dimensions a = 11.958 (3), b = 6.924 (2), c = 8.317 (2) Å, β = 96.16 (2)°, and V = 684.7 Å^3 at 24 (1)° were obtained as described above using the diffractometer. Due to the instability of the crystals, no density information was obtained except that the crystals sank in water and floated in iodoethane (density 1.99 g cm^{-3}). No piezoelectric test was performed.

Of 1306 independent reflections collected in the range 4° < 2θ < 50° using a 2.5° scan, 1168 reflections were used in refinement, the remainder being rejected according to the criterion stated above.

A three-dimensional sharpened Patterson synthesis showed (unambiguously) the presence of only two germanium atoms in the unit cell and a three-dimensional Fourier synthesis phased by germanium only placed at y = 0.25 (R = 51.8%) showed the remaining nonhydrogen atoms of the structure, including four maxima interpreted as nitromethane in a 1:1 ratio with the germanium complex. Except the two "axial" fluorine atoms, all peaks were centered on the section y = 0.25; thus refinement was commenced using the centrosymmetric space group $P2_1/m$ with Z = 2; *i.e.*, both complex and solvent of crystallization constrained to possess mirror symmetry. Least-squares refine-

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[24] Fourier and Patterson summations were obtained using FORDAP by A. Zalkin suitably modified to run on a CDC 3300.

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[26] A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-1402. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

Table I: Final Positions[a] and Thermal Parameters[b] with Esd's[c] (Estmated Standard Deviations)

Atom	x	y	z	B or B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
(A) $SiF_4C_{10}H_8N_2$									
Si	−0.39318 (20)	0.22561 (17)	−0.12231 (9)	1,223.1 (33)	1,131.9 (21)	293.7 (6)	47.2 (22)	104.9 (11)	166.6 (10)
F1	−0.3212 (4)	0.3523 (3)	−0.1767 (2)	4,973 (9)	2,563 (5)	786 (1)	80 (5)	525 (3)	280 (2)
F2	−0.4267 (4)	0.0920 (3)	−0.0615 (2)	1,408 (7)	1,562 (5)	388 (1)	−263 (5)	152 (2)	307 (2)
F3	−0.5671 (4)	0.1701 (3)	−0.2021 (2)	1,396 (6)	1,533 (5)	381 (1)	25 (5)	−110 (2)	117 (2)
F4	−0.5208 (4)	0.3420 (4)	−0.0867 (2)	1,963 (8)	1,857 (5)	441 (1)	687 (5)	262 (3)	119 (2)
N1	−0.1551 (6)	0.2712 (4)	−0.0315 (2)	1,654 (10)	1,022 (6)	246 (2)	−336 (7)	165 (3)	55 (3)
N2	−0.2051 (5)	0.0965 (4)	−0.1523 (2)	1,184 (9)	870 (6)	244 (2)	−91 (6)	31 (3)	135 (3)
C1	−0.1514 (9)	0.3631 (6)	0.0312 (3)	2,765 (17)	1,129 (9)	309 (2)	−126 (9)	333 (5)	34 (4)
C2	0.0230 (10)	0.3895 (6)	0.0928 (3)	3,678 (21)	1,098 (8)	293 (2)	−590 (11)	330 (6)	−46 (4)
C3	0.1891 (9)	0.3224 (7)	0.0892 (3)	2,224 (16)	1,474 (10)	266 (2)	−535 (10)	0 (5)	−11 (4)
C4	0.1851 (7)	0.2282 (6)	0.0261 (3)	1,479 (13)	1,149 (8)	299 (2)	−383 (8)	−35 (4)	86 (4)
C5	0.0092 (7)	0.2036 (5)	−0.0337 (3)	1,279 (11)	899 (7)	248 (2)	−53 (7)	145 (4)	84 (3)
C6	−0.0209 (6)	0.1015 (5)	−0.1041 (3)	910 (11)	907 (7)	210 (2)	−282 (7)	10 (4)	89 (3)
C7	0.1264 (7)	0.0205 (6)	−0.1217 (3)	1,379 (13)	1,138 (8)	357 (2)	−205 (8)	312 (5)	119 (4)
C8	0.0776 (8)	−0.0703 (6)	−0.1898 (3)	2,044 (15)	1,234 (8)	364 (2)	−95 (9)	417 (5)	−24 (4)
C9	−0.1136 (8)	−0.0796 (6)	−0.2383 (3)	2,120 (15)	1,206 (8)	355 (2)	−180 (9)	298 (5)	−82 (4)
C10	−0.2532 (8)	0.0023 (6)	−0.2183 (3)	1,800 (14)	1,073 (8)	274 (2)	−386 (9)	41 (5)	−13 (4)
H1	−0.2831	0.4164	0.0339	5.0					
H2	0.0261	0.4632	0.1432	5.0					
H3	0.3242	0.3437	0.1364	5.0					
H4	0.3158	0.1740	0.0227	5.0					
H7	0.2748	0.0289	−0.0829	5.0					
H8	0.1883	−0.1342	−0.2052	5.0					
H9	−0.1528	−0.1508	−0.2917	5.0					
H10	−0.4030	−0.0076	−0.2551	5.0					
(B) $GeF_4C_{10}H_8N_2 \cdot CH_3NO_2$									
Ge	0.22955 (4)	0.2500	−0.22420 (6)	363.0 (4)	2,043.4 (16)	594.8 (8)	0	57.6 (4)	0
F1	0.2308 (2)	0.5062 (3)	−0.2121 (2)	725 (2)	1,967 (6)	1,725 (4)	126 (3)	153 (2)	663 (4)
F3	0.1018 (3)	0.2500	−0.3510 (3)	493 (2)	4,942 (13)	968 (5)	0	−94 (3)	0
F4	0.3168 (3)	0.2500	−0.3811 (3)	642 (3)	5,006 (14)	786 (4)	0	297 (3)	0
N1	0.3619 (3)	0.2500	−0.0509 (4)	407 (3)	1,328 (10)	872 (6)	0	123 (3)	0
N2	0.1488 (3)	0.2500	−0.0217 (4)	353 (3)	1,500 (10)	851 (6)	0	70 (3)	0
C1	0.4701 (4)	0.2500	−0.0827 (6)	357 (3)	1,489 (13)	1,410 (8)	0	142 (4)	0
C2	0.5563 (4)	0.2500	0.0420 (7)	431 (4)	1,688 (14)	1,759 (10)	0	25 (5)	0
C3	0.5321 (5)	0.2500	0.1991 (7)	516 (4)	2,454 (17)	1,457 (9)	0	−176 (5)	0
C4	0.4206 (4)	0.2500	0.2329 (6)	525 (4)	2,547 (17)	1,066 (8)	0	−149 (4)	0
C5	0.3367 (4)	0.2500	0.1025 (5)	447 (4)	1,408 (12)	834 (7)	0	10 (4)	0
C6	0.2144 (4)	0.2500	0.1192 (5)	457 (4)	1,588 (12)	749 (7)	0	46 (4)	0
C7	0.1697 (5)	0.2500	0.2660 (6)	643 (4)	2,543 (17)	872 (7)	0	229 (4)	0
C8	0.0529 (5)	0.2500	0.2631 (7)	733 (5)	2,762 (18)	1,431 (10)	0	571 (6)	0
C9	−0.0144 (5)	0.2500	0.1185 (7)	503 (4)	2,052 (15)	1,507 (9)	0	322 (5)	0
C10	0.0356 (4)	0.2500	−0.0230 (6)	384 (4)	1,873 (14)	1,276 (8)	0	123 (4)	0
CMe	0.8187 (5)	0.2500	−0.4641 (7)	871 (5)	3,735 (22)	1,142 (9)	0	352 (5)	0
NMe	0.7387 (5)	0.2500	−0.3398 (6)	742 (4)	2,810 (15)	1,406 (8)	0	201 (5)	0
OA	0.7752 (5)	0.2500	−0.2002 (6)	1,250 (5)	7,316 (27)	1,151 (7)	0	236 (5)	0
OB	0.6411 (5)	0.2500	−0.3836 (7)	745 (5)	11,108 (41)	2,751 (12)	0	288 (6)	0
H1	0.4895	0.2500	−0.2066	5.0					
H2	0.6427	0.2500	0.0155	5.0					
H3	0.5994	0.2500	0.2967	5.0					
H4	0.3997	0.2500	0.3560	5.0					
H7	0.2235	0.2500	0.3789	5.0					
H8	0.0151	0.2500	0.3753	5.0					
H9	−0.1049	0.2500	0.1158	5.0					
H10	−0.0165	0.2500	−0.1374	5.0					
(C) $SnF_4C_{10}H_8N_2 \cdot CH_3NO_2$									
Sn	0.23940 (4)	0.00608 (3)	0.23531 (2)	1,143.5 (5)	488.8 (3)	253.9 (2)	−75.6 (3)	44.7 (2)	−9.5 (2)
F1	0.0630 (3)	0.1058 (2)	0.2385 (2)	1,284 (4)	688 (3)	646 (2)	242 (3)	−177 (2)	105 (2)
F2	0.4138 (3)	−0.0954 (3)	0.2461 (2)	1,419 (5)	928 (3)	678 (2)	364 (3)	266 (3)	−182 (2)
F3	0.3267 (4)	0.1036 (3)	0.1389 (2)	2,277 (6)	1,162 (3)	347 (2)	−792 (4)	128 (3)	130 (2)
F4	0.1324 (4)	−0.0957 (3)	0.1419 (2)	2,060 (6)	901 (3)	383 (2)	−537 (3)	−58 (2)	−149 (2)
N1	0.1593 (4)	−0.0791 (3)	0.3664 (2)	874 (5)	412 (3)	320 (2)	58 (3)	47 (3)	12 (2)
N2	0.3438 (4)	0.1010 (3)	0.3625 (2)	820 (5)	443 (3)	294 (2)	68 (3)	39 (3)	−20 (2)
C1	0.0650 (5)	−0.1697 (4)	0.3606 (3)	1,122 (7)	406 (3)	482 (3)	−8 (4)	121 (4)	−3 (2)
C2	0.0121 (6)	−0.2180 (4)	0.4456 (4)	1,300 (8)	462 (4)	551 (3)	−13 (4)	231 (4)	91 (3)
C3	0.0624 (6)	−0.1746 (4)	0.5372 (4)	1,216 (7)	552 (4)	517 (3)	144 (5)	247 (4)	157 (3)
C4	0.1584 (5)	−0.0813 (4)	0.5438 (3)	1,069 (7)	526 (4)	369 (3)	188 (4)	86 (3)	72 (2)
C5	0.2080 (5)	−0.0355 (4)	0.4551 (3)	767 (6)	454 (3)	267 (2)	189 (3)	87 (3)	9 (2)
C6	0.3120 (5)	0.0641 (3)	0.4540 (3)	699 (6)	435 (3)	253 (2)	217 (3)	61 (3)	−29 (2)
C7	0.3791 (5)	0.1170 (4)	0.5387 (3)	765 (6)	547 (4)	357 (3)	88 (4)	59 (3)	−83 (2)
C8	0.4774 (5)	0.2084 (4)	0.5283 (3)	1,099 (7)	589 (4)	421 (3)	56 (4)	−13 (4)	−189 (3)
C9	0.5093 (5)	0.2449 (4)	0.4344 (4)	1,029 (7)	563 (4)	471 (3)	−122 (4)	75 (4)	−69 (3)
C10	0.4400 (5)	0.1899 (4)	0.3521 (3)	1,075 (7)	495 (4)	432 (3)	−75 (4)	91 (4)	12 (3)
CMe	0.2286 (9)	0.0044 (5)	−0.0723 (5)	2,921 (15)	1,277 (7)	393 (3)	−56 (8)	128 (6)	−9 (4)
NMe	0.2536 (5)	−0.0087 (5)	−0.1790 (4)	1,154 (6)	1,116 (5)	492 (3)	−124 (5)	−32 (3)	−44 (3)
OA	0.2293 (5)	0.0733 (5)	−0.2332 (3)	1,656 (7)	1,560 (6)	685 (3)	−110 (5)	7 (4)	378 (4)
OB	0.2965 (5)	−0.1024 (5)	−0.2074 (4)	1,871 (8)	1,517 (6)	1,038 (4)	348 (6)	42 (5)	−377 (4)
H1	0.0299	−0.2054	0.2882	5.0					
H2	−0.0675	−0.2885	0.4397	5.0					
H3	0.0269	−0.2142	0.6048	5.0					
H4	0.1952	−0.0449	0.6153	5.0					
H7	0.3554	0.0874	0.6121	5.0					
H8	0.5287	0.2510	0.5937	5.0					
H9	0.5869	0.3149	0.4256	5.0					
H10	0.4628	0.2193	0.2783	5.0					

[a] Hydrogen atoms are placed 1.08 Å from the carbon atom to which they are bonded. [b] Anisotropic thermal parameters have been multiplied by 10^5. [c] Esd's are shown in parentheses. They are right-justified to the least significant digit of the preceding number.

ment of individual positional and isotropic thermal parameters commenced with $R = 34.4\%$ and $R_w = 38.1\%$ and converged after five cycles with $R = 10.8\%$ and $R_w = 11.1\%$.

A Fourier synthesis based on the difference between observed and calculated structure factors at this stage showed the hydrogen atoms of the bipyridyl ligand (peak heights $\simeq 0.4$ e/Å^3); however, the methyl hydrogen atoms of the nitromethane were not recognizable. The presence of these features, together with imperfections in the map in the region of the isotropically refined atoms, suggested that the structural model might be improved by the inclusion of parameters corresponding to the bipyridyl hydrogen atoms placed in calculated positions and by the use of anisotropic thermal parameters for the nonhydrogen atoms. A new convergence with $R = 3.8\%$, $R_w = 5.0\%$, and a "goodness of fit" parameter of 1.168 was obtained after six cycles of full-matrix refinement, using individual anisotropic parameters with b_{12} and b_{23} constrained to zero as the symmetry of the space group requires. Before this phase of refinement the data were corrected for absorpion of X-rays by the crystal (volume 0.021 mm^3, $\mu = 24.22$ cm^{-1}); the transmission coefficients ranged from 0.48 to 0.70. Also the scattering factor for neutral germanium was corrected for anomalous dispersion ($\Delta f'$(Ge) = 0.2 e and $\Delta f''$(Ge) = 1.9 e for Mo Kα radiation).

A final difference Fourier synthesis showed no peaks representing more than 0.2 e/Å^3 even in the vicinity of the methyl group. Examination of the refined anisotropic vibration ellipsoids shows no particular trend for the major axis to be perpendicular to the mirror plane and on this basis an attempt at refinement in space group $P2_1$ was deemed unjustifiable. Table IB shows the final atomic parameters.[26]

$SnF_4C_{10}H_8N_2 \cdot CH_3NO_2$.—The selection and preparation of a suitable crystal, unit cell determination, and structure solution and refinement were essentially identical with the procedures described for the germanium complex. The space group was uniquely determined photographically as $P2_1/c$ (no. 14) and refined unit cell parameters are $a = 8.844$ (2), $b = 11.646$ (4), $c = 13.420$ (5) Å, $\beta = 94.04$ (2)°, and $V = 1378.9$ Å^3; 2415 unique diffraction intensities were measured and 2077 were used in subsequent computations.

The initial Fourier synthesis ($R = 36.6\%$) revealed the entire structure except the hydrogen atoms. Isotropic refinement was terminated at $R = 10.6\%$, $R_w = 10.9\%$. After correction for absorption of X-rays by the crystal (irregularly shaped, *ca.* 0.30 × 0.17 × 0.17 mm, volume 0.018 mm^3, $\mu = 19.08$ cm^{-1}, transmission coefficients 0.58–0.75), inclusion of hydrogen atoms on the bipyridyl moiety in calculated positions (not refined but recalculated between cycles), and correction for anomalous dispersion by tin ($\Delta f' = -0.6$ e and $\Delta f'' = 1.9$ e), further refinement using anisotropic thermal parameters reduced R to 3.2% and R_w to 4.0%. The "goodness of fit" parameter was 0.89 and the residual electron density on a difference Fourier summation compiled at the completion of refinement did not exceed 0.3 e/Å^3. Final atomic parameters are displayed in Table IC.[26]

The Crystal and Molecular Structures

All three structures are monomeric and show the expected octahedral coordination of the central atom. No displacement of the bipyridyl ligand by nitromethane from the first coordination sphere of the germanium and tin atoms has occurred on recrystallization. Table II gives details of the molecular geometries, and an analysis of the atomic thermal parameters summarized in Table III is shown graphically in Figures 1–3. The more important intermolecular contacts are collected in Table IV and the molecular packing is depicted in Figures 4–6.

A comparison of the three structures is not valid without first establishing the degree of distortion of the molecular geometries from their isolated conformation by crystal-packing effects. Using the sums of van der Waals radii[27] as an indication of close contact, only distances between fluorine atoms and the hydrogen atoms of another complex molecule or nitromethane appear unduly short. The shortest of such contacts, 2.155 Å, appears between F2 (an axial fluorine atom) and H7 in the crystal lattice of $SiF_4C_{10}H_8N_2$. This is 0.3 Å shorter than the radius sum of 2.55 Å, representing

TABLE II

INTERMOLECULAR BOND DISTANCES AND ANGLES

Atom 1–atom 2	Distances and esd's,[a] Å		
(M = Si, Ge, or Sn)	$SiF_4C_{10}H_8N_2$	$GeF_4C_{10}H_8N_2$	$SnF_4C_{10}H_8N_2$
M–F1	1.654 (3)	1.777 (2)	1.948 (3)
M–F2[b]	1.659 (3)	1.777 (2)	1.940 (3)
M–F3	1.629 (3)	1.761 (3)	1.924 (3)
M–F4	1.632 (3)	1.757 (3)	1.925 (3)
M–N1	1.982 (4)	2.023 (4)	2.181 (3)
M–N2	1.972 (4)	2.029 (4)	2.183 (3)
N1–C1	1.345 (7)	1.349 (6)	1.343 (6)
C1–C2	1.397 (9)	1.382 (7)	1.383 (7)
C2–C3	1.361 (9)	1.369 (8)	1.374 (7)
C3–C4	1.363 (8)	1.392 (8)	1.378 (7)
C4–C5	1.388 (7)	1.396 (7)	1.403 (6)
C5–N1	1.345 (6)	1.342 (6)	1.337 (5)
C5–C6	1.476 (7)	1.485 (7)	1.481 (6)
C6–N2	1.339 (6)	1.338 (6)	1.348 (5)
C6–C7	1.395 (7)	1.384 (7)	1.390 (6)
C7–C8	1.378 (8)	1.395 (8)	1.387 (6)
C8–C9	1.384 (8)	1.373 (8)	1.377 (7)
C9–C10	1.372 (8)	1.377 (7)	1.383 (7)
C10–N2	1.370 (7)	1.352 (6)	1.354 (6)
H4···H7	2.172	2.132	2.091
N1···N2	2.532 (6)	2.585 (5)	2.660 (5)
CMe–NMe		1.483 (8)	1.471 (8)
NMe–OA		1.196 (7)	1.211 (7)
NMe–OB		1.185 (8)	1.225 (8)

Atom 1–atom 2–atom 3	Angles at atom 2 and esd's, deg		
(M = Si, Ge, Sn)	$SiF_4C_{10}H_8N_2$	$GeF_4C_{10}H_8N_2$	$SnF_4C_{10}H_8N_2$
F1–M–F2	170.5 (2)	173.6 (1)	174.4 (1)
F1–M–F3	93.0 (2)	92.0 (1)	91.3 (1)
F1–M–F4	92.4 (2)	92.3 (1)	91.4 (1)
F1–M–N1	86.5 (2)	87.6 (1)	87.0 (1)
F1–M–N2	86.2 (2)	87.4 (1)	88.6 (1)
F2–M–F3	93.6 (2)	92.0 (1)	93.2 (1)
F2–M–F4	93.5 (2)	92.3 (1)	91.4 (1)
F2–M–N1	85.9 (2)	87.6 (1)	87.9 (1)
F2–M–N2	86.9 (2)	87.4 (1)	87.7 (1)
F3–M–F4	97.4 (2)	95.9 (1)	97.3 (1)
F3–M–N1	170.9 (2)	171.4 (1)	168.4 (1)
F3–M–N2	91.2 (2)	92.1 (1)	93.4 (1)
F4–M–N1	91.8 (2)	92.7 (1)	94.2 (1)
F4–M–N2	171.4 (2)	172.0 (1)	169.3 (1)
N1–M–N2	79.7 (2)	79.3 (1)	75.1 (1)
M–N1–C5	116.8 (3)	116.1 (3)	116.3 (3)
N1–C5–C6	112.9 (4)	114.4 (4)	116.8 (3)
C5–C6–N2	113.4 (4)	114.1 (4)	115.3 (3)
C6–N2–M	117.1 (3)	116.2 (3)	116.5 (3)
C1–N1–C5	119.6 (4)	120.3 (4)	120.6 (4)
N1–C1–C2	120.0 (5)	120.5 (5)	121.1 (4)
C1–C2–C3	120.0 (5)	120.0 (5)	118.8 (4)
C2–C3–C4	120.1 (5)	119.9 (5)	120.4 (5)
C3–C4–C5	118.5 (5)	117.9 (5)	118.3 (4)
C4–C5–C6	125.1 (4)	124.1 (4)	122.5 (4)
C4–C5–N1	121.9 (4)	121.5 (4)	120.7 (4)
N2–C6–C7	122.2 (4)	121.8 (4)	120.0 (4)
C5–C6–C7	124.4 (4)	124.0 (4)	124.7 (4)
C6–C7–C8	118.2 (5)	117.7 (5)	119.4 (4)
C7–C8–C9	120.0 (5)	120.5 (5)	120.0 (4)
C8–C9–C10	119.6 (5)	118.7 (5)	118.7 (4)
C9–C10–N2	120.9 (5)	121.3 (5)	121.2 (4)
C6–N2–C10	119.1 (4)	119.9 (4)	120.7 (4)
CMe–NMe–OA		118.8 (5)	118.1 (5)
CMe–NMe–OB		118.3 (5)	117.8 (5)
OA–NMe–OB		122.9 (6)	124.1 (5)

[a] The estimated standard deviations shown in parentheses are right-adjusted to the least significant digit of the preceding number. They are computed from the diagonal elements of the inverted least-squares matrix and do not include contributions from cell constant errors. [b] F2 is generated from F1 in the case of $GeF_4C_{10}H_8N_2$ by the operation $x, {}^1/_2 - y, z$.

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(27) L. Pauling, "The Nature of the Chemical Bond," 2nd ed, Cornell University Press, Ithaca, N. Y., 1945, p 187.

TABLE III: THERMAL VIBRATION ELLIPSOIDS[a]

Atom	Major axis *(direction cosines)*	Median axis *(direction cosines)*	Minor axis *(direction cosines)*
(A) $SiF_4C_{10}H_8N_2$			
Si1	4.57	2.67	2.15
	(1895, −7985, −5715)	(7379, 4997, −4537)	(6478, −3357, 6838)
F1	10.17	9.48	6.71
	(3788, −7131, −5899)	(9237, 2518, 2887)	(−0574, −6542, 7541)
F2	6.98	2.91	2.26
	(3047, −7881, −5349)	(4983, −3467, 7947)	(8118, 5086, −2871)
F3	5.97	4.72	1.99
	(4772, −6249, −6180)	(4943, 7722, −3992)	(7267, −1150, 6773)
F4	7.17	4.57	2.84
	(4056, 8885, 2142)	(3346, 0737, −9395)	(8506, −4529, 2674)
N1	4.35	2.65	2.19
	(6432, −7531, −1391)	(4850, 2599, 8350)	(5927, 6044, −5324)
N2	3.99	2.25	1.82
	(4875, −6597, −5721)	(7764, 6273, −0619)	(3996, −4140, 8179)
C1	5.32	3.85	2.94
	(9475, −2175, 2345)	(1129, 9135, 3908)	(2993, 3438, −8901)
C2	7.63	3.14	2.93
	(9229, −3571, 1442)	(3801, 9052, −1902)	(−0627, 2303, 9711)
C3	6.39	3.87	2.33
	(7088, −6894, −1499)	(5632, 6808, −4684)	(4249, 2476, 8707)
C4	5.40	2.99	2.04
	(6322, −6353, −4436)	(2635, 7146, −6480)	(7286, 2928, 6191)
C5	3.44	2.41	2.23
	(3003, −8124, −4998)	(8757, 0270, 4820)	(3782, 5824, −7196)
C6	3.93	1.96	1.39
	(5019, −7649, −4038)	(−2111, −5610, 8005)	(8388, 3165, 4429)
C7	4.54	3.50	1.82
	(1820, −7883, −5878)	(4930, −4441, 7482)	(8509, 4258, −3079)
C8	4.56	4.01	2.78
	(5433, −5348, 6472)	(2935, 8432, 4503)	(7865, 0547, −6151)
C9	4.64	3.66	3.34
	(4903, −7131, 5009)	(8674, 4551, −2013)	(−0845, 5333, 8417)
C10	4.86	3.23	2.24
	(7651, −6021, −2286)	(3168, 6607, −6805)	(5607, 4482, 6962)
(B) $GeF_4C_{10}H_8N_2 \cdot CH_3NO_2$			
Ge1	3.92	2.05	1.62
	(0000, 10,000, 0000)	(9926, 0000, 1218)	(1218, 0000, −9926)
F1	5.86	4.06	2.64
	(1261, 5926, 7956)	(9867, 0077, −1621)	(1021, −8055, 5838)
F3	9.48	3.47	2.11
	(0000, 10,000, 0000)	(7777, 0000, −6286)	(6286, 0000, 7777)
F4	9.60	3.94	1.65
	(0000, 10,000, 0000)	(8848, 0000, 4659)	(4659, 0000, −8848)
N1	2.55	2.55	2.08
	(5978, 0000, 8017)	(0000, 10,000, 0000)	(8017, 0000, −5978)
N2	2.88	2.33	1.98
	(0000, 10,000, 0000)	(0704, 0000, 9975)	(9975, 0000, −0704)
C1	3.87	2.86	1.96
	(0763, 0000, 9971)	(0000, 10,000, 0000)	(9971, 0000, −0763)
C2	4.89	3.24	2.42
	(1738, 0000, −9848)	(0000, 10,000, 0000)	(9848, 0000, 1738)
C3	4.77	4.71	2.36
	(5718, 0000, −8204)	(0000, 10,000, 0000)	(8204, 0000, 5718)
C4	4.88	3.96	2.12
	(0000, 10,000, 0000)	(7539, 0000, −6570)	(6570, 0000, 7539)
C5	2.70	2.68	2.17
	(0000, 10,000, 0000)	(8880, 0000, −4599)	(4599, 0000, 8880)
C6	3.04	2.60	2.05
	(0000, 10,000, 0000)	(9976, 0000, −0692)	(0692, 0000, 9976)
C7	4.88	3.81	2.09
	(0000, 10,000, 0000)	(9101, 0000, 4144)	(4144, 0000, −9101)
C8	5.67	5.30	1.99
	(6913, 0000, 7226)	(0000, 10,000, 0000)	(7226, 0000, −6913)
C9	4.49	3.93	2.28
	(4098, 0000, 9122)	(0000, 10,000, 0000)	(9122, 0000, −4098)
C10	3.59	3.50	2.12
	(0000, 10,000, 0000)	(0784, 0000, 9969)	(9969, 0000, −0784)
CMe	7.16	5.24	2.60
	(0000, 10,000, 0000)	(8953, 0000, 4454)	(4454, 0000, −8953)
NMe	5.39	4.38	3.58
	(0000, 10,000, 0000)	(8175, 0000, 5759)	(5759, 0000, −8175)
OA	14.03	7.08	3.06
	(0000, 10,000, 0000)	(9888, 0000, 1494)	(1494, 0000, −9888)
OB	21.30	7.56	4.07
	(0000, 10,000, 0000)	(0937, 0000, 9956)	(9956, 0000, −0937)

TABLE III (*Continued*)

Atom	Major axis (direction cosines)	Median axis (direction cosines)	Minor axis (direction cosines)
		(C) $SnF_4C_{10}H_8N_2 \cdot CH_3NO_2$	
Sn1	3.66 (9540, −2950, 0529)	2.56 (2976, 9538, −0428)	1.81 (−0378, 0566, 9977)
F1	2.82 (9104, 3811, 1609)	2.30 (2567, −2154, −9422)	2.12 (3244, −8991, 2939)
F2	3.78 (7019, −0273, 7117)	3.12 (7118, −0099, −7023)	2.20 (0262, 9996, 0125)
F3	4.81 (6653, 1511, 7311)	3.36 (7054, −4481, −5492)	2.22 (2447, 8811, −4047)
F4	5.13 (5789, 4518, 6788)	2.93 (8079, −4306, −4025)	2.30 (1105, 7814, −6142)
N1	4.01 (7334, 6003, 3191)	2.64 (5545, −2567, −7916)	2.16 (3932, −7575, 5211)
N2	3.22 (6838, 7086, 1742)	1.96 (2175, −4258, 8783)	1.54 (6965, −5627, −4453)
C1	9.12 (9921, −1071, 0651)	6.90 (1076, 9942, −0051)	2.79 (−0642, 0120, 9979)
C2	6.17 (1804, −9806, 0771)	3.98 (7207, 0784, −6888)	3.08 (6694, 1799, −7208)
C3	9.75 (1521, −8844, −4412)	5.09 (9884, 1370, 0661)	3.74 (0020, −4461, 8950)
C4	10.67 (2919, 7577, −5836)	6.19 (6677, 2755, 6916)	4.68 (6849, −5916, −4255)
C5	5.60 (6577, 0731, −7497)	4.64 (4317, 7790, 4547)	2.29 (6172, −6228, 4808)
C6	6.40 (4707, 8193, −3275)	5.53 (5833, −0104, 8122)	2.25 (6621, −5733, −4828)
C7	10.03 (7427, −6690, −0293)	3.89 (5777, 6180, 5331)	1.92 (3386, 4129, −8455)
C8	7.99 (8175, −5752, 0289)	4.16 (4781, 6497, −5910)	1.98 (3212, 4970, 8061)
C9	2.78 (7776, 6236, −0806)	2.27 (5416, −5992, 5896)	2.01 (3194, −5021, −8037)
C10	3.17 (6634, 7480, −0224)	1.92 (3079, −2456, 9192)	1.24 (6820, −6167, −3932)
CMe	3.41 (2727, 8304, −4859)	2.54 (7233, 1561, 6727)	1.95 (6345, −5348, −5581)
NMe	4.47 (3845, 6774, −6272)	3.29 (9231, −2776, 2661)	1.92 (−0062, 6813, 7320)
OA	3.90 (5046, −6041, 6168)	3.17 (6887, −1492, −7095)	2.54 (5207, 7828, 3407)
OB	3.52 (8740, −2984, 3835)	3.06 (2578, −3842, −8866)	2.51 (4119, 8737, −2588)

[a] The major, median, and minor axes of the thermal vibration ellipsoid are quoted in units corresponding to the usual isotropic thermal parameter B, *i.e.*, the root-mean-square displacement $(\bar{U}^2)^{1/2} = (B/8\pi^2)^{1/2}$. The direction cosines, given in parentheses below each axis length, are multiplied by 10^4.

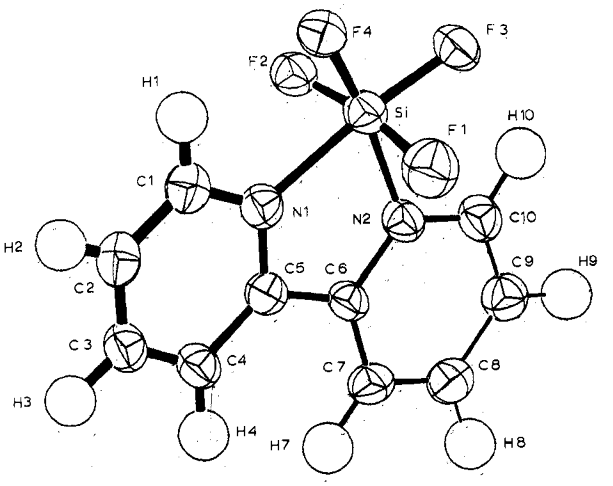

Figure 1.—Molecular structure of $SiF_4C_{10}H_8N_2$ projected down [010] showing 68% probability envelopes of the vibration ellipsoids.

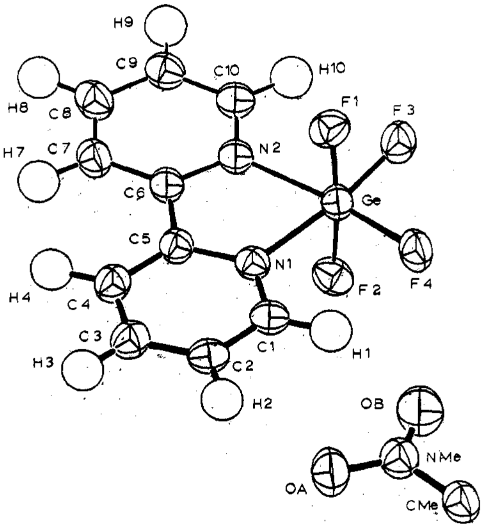

Figure 2.—Molecular structure of $GeF_4C_{10}H_8N_2 \cdot CH_3NO_2$ projected down [110].

at best a very weak[28] and chemically improbable hydrogen bond. The other axial fluorine atom (F1) is 2.364 Å distant from H10 of a different neighboring molecule; however, relative to the symmetry of the isolated molecule, the orientation of this contact is

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[28] W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968, p 16.

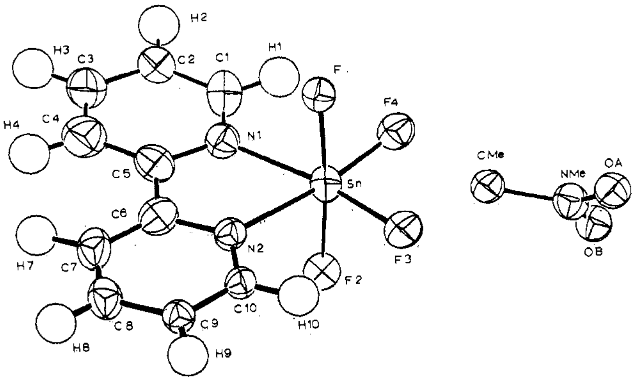

Figure 3.—Molecular structure of $SnF_4C_{10}H_8N_2 \cdot CH_3NO_2$ projected down [010].

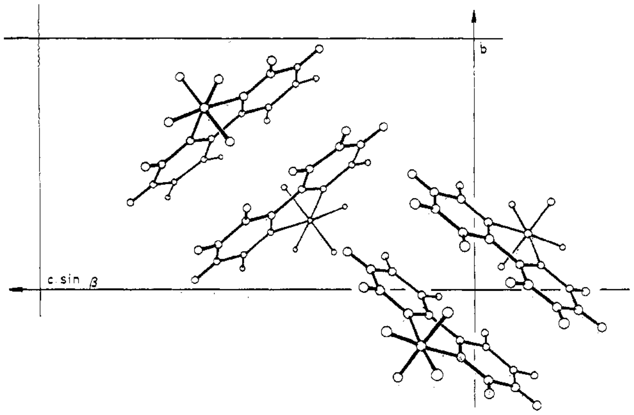

Figure 4.—Crystal packing of $SiF_4C_{10}H_8N_2$ projected down [100].

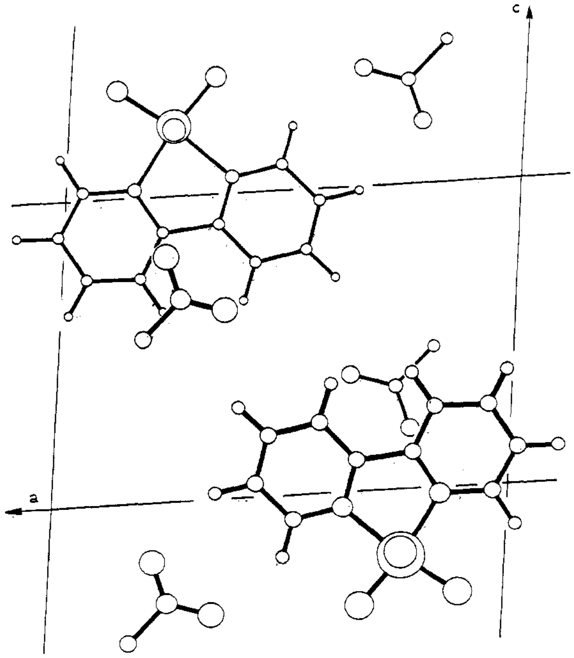

Figure 5.—Crystal packing of $GeF_4C_{10}H_8N_2 \cdot CH_3NO_2$ projected down [010].

TABLE IV
INTERMOLECULAR CONTACTS (Å)[a]

$SiF_4C_{10}H_8N_2$

H7···F2	2.155 (VIII)[b]	H2···F1	2.646 (VI)
H10···F1	2.364 (I)	H2···C9	2.700 (III)
H8···F1	2.444 (II)	H3···H10	2.715 (V)
H2···H9	2.578 (III)	H4···F2	2.740 (VIII)
H9···F3	2.580 (I)	H3···F1	2.875 (VI)
H4···F2	2.594 (IV)	H7···F3	2.877 (VIII)
H3···F3	2.602 (V)	H2···C8	2.898 (III)
H7···F2	2.606 (IV)	H1···F4	2.903 (VII)
H9···F4	2.630 (I)	H10···F4	2.905 (I)
		H8···H2	2.934 (III)

(I) $-x, -\frac{1}{2} + y, -\frac{1}{2} - z$
(II) $1 - x, -\frac{1}{2} + y, -\frac{1}{2} - z$
(III) $x, \frac{1}{2} - y, \frac{1}{2} + z$
(IV) $-x, -y, -z$
(V) $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$
(VI) $-x, 1 - y, -z$
(VII) $-1 - x, 1 - y, -z$
(VIII) $1 + x, y, z$

$GeF_4C_{10}H_8N_2 \cdot CH_3NO_2$

H7···F3	2.177 (III)	H3···F1	2.784 (VII)
H8···F4	2.399 (III)	H7···F4	2.806 (III)
H1···OB	2.450 (IV)	H8···CME	2.822 (II)
H9···F1	2.452 (V)	H9···OA	2.854 (I)
H10···OA	2.489 (I)	H3···CME	3.116 (III)
H4···F3	2.494 (III)	F1···CME	3.179 (VI)
H2···OA	2.520 (IV)	H10···CME	3.181 (I)
H3···OB	2.655 (III)	F4···CME	3.414 (I)
H2···F1	2.697 (VII)		

(I) $-1 + x, y, z$
(II) $-1 + x, y, 1 + z$
(III) $x, y, 1 + z$
(IV) x, y, z
(V) $-x, -\frac{1}{2} + y, -z$
(VI) $1 - x, 1 - y, -1 - z$
(VII) $1 - x, 1 - y, -z$

$SnF_4C_{10}H_8N_2 \cdot CH_3NO_2$

H1···F1	2.367 (VII)	H2···F1	2.697 (VII)
H7···OA	2.427 (II)	H8···OB	2.703 (VIII)
H3···F4	2.445 (IX)	H10···OB	2.745 (V)
H4···OA	2.453 (II)	H2···F3	2.761 (VII)
H10···F2	2.458 (VIII)	H4···NMe	2.803 (II)
H9···F2	2.526 (VIII)	H1···OA	2.815 (III)
H8···F3	2.568 (X)	H8···F2	2.829 (VI)
H4···OB	2.574 (II)	H9···F4	2.893 (VIII)
H8···H10	2.607 (X)	F3···CMe	3.127 (I)
H3···F1	2.623 (IV)	F4···CMe	3.270 (I)
H3···H1	2.639 (IX)	H2···CMe	3.369 (VII)
H7···F2	2.695 (VI)	F4···CMe	3.432 (III)

(I) x, y, z
(II) $x, y, 1 + z$
(III) $-x, -y, -z$
(IV) $-x, -y, 1 - z$
(V) $1 - x, -y, -z$
(VI) $1 - x, -y, 1 - z$
(VII) $-x, -\frac{1}{2} + y, \frac{1}{2} - z$
(VIII) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
(IX) $x, -\frac{1}{2} - y, \frac{1}{2} + z$
(X) $x, \frac{1}{2} - y, \frac{1}{2} + z$

[a] Only interatomic distances less than 3.0 Å are given, except where methyl group carbon atoms are involved, in which case the limit is raised to 3.5 Å. [b] Transformations given below each group of distances indicate the position of the second atom relative to the coordinates given in Table IA, B, and C.

quite different. For strong interactions in dissimilar orientations, distortion of the molecular geometry might be expected; however this was not observed. Chemically, the methyl hydrogen atoms of the nitromethane present in the germanium and tin structures are more likely to be implicated in hydrogen bonding. However, assuming a maximum van der Waals radius of 2 Å for a methyl group, no short intermolecular distances occur; nor was there any indication on final difference Fourier syntheses that the rotation of the methyl group was restricted. In addition, the nitromethane is very easily lost from the lattice. On the other hand, the complexes are only soluble in potentially hydrogen-bonding solvents so the possibility of significant intermolecular forces cannot be completely discounted. Finally, a comparison of the three structures reveals no structural peculiarity which might be symptomatic of significant packing forces (Figure 7).

The Coordination of the Silicon, Germanium, and

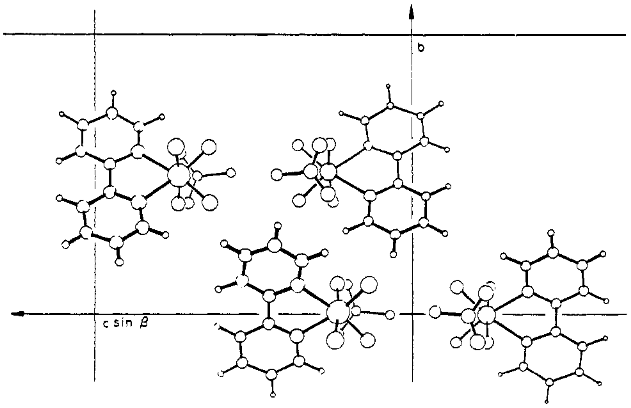

Figure 6.—Crystal packing of $SnF_4C_{10}H_8N_2 \cdot CH_3NO_2$ projected down [100].

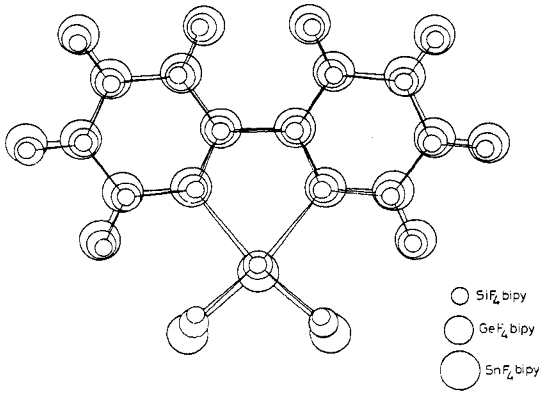

Figure 7.—Superimposed projections of $MF_4C_{10}H_8N_2$ molecules (where M = Si, Ge, and Sn). Giving all atoms except hydrogen unit weight, the centers of gravity are coincident.

Tin Atoms.—Two types of distortion from regular octahedral symmetry are of interest: differences in potentially equal bond lengths and angular distortions. Unfortunately, there have been no really comparable crystal structures reported; the only other fluoride complex studied is bis(pyridine)tetrafluorosilicon(IV),[3] which is trans octahedral with no structural anomalies either expected or discovered.

In a recent report of the structure of trichloroterpyridylgallium(III) a significant (*ca.* 0.13 Å) difference between axial and equatorial Ga–Cl bond distances was ascribed to a trans effect presumably involving d_π–d_π bonding between the filled 3d orbitals of gallium and the empty 3d orbitals of chlorine. The present study might have revealed effects attributable to p_π–d_π bonding where the filled 2p orbitals of equatorial fluorines act as π donors to the empty d orbitals of the central atom more effectively than those of the axial fluorine atoms. In fact, a comparatively insignificant difference is observed: the distances to axial fluorine atoms are 0.025 (4), 0.010 (3), and 0.020 (4) Å longer than the equatorial distances for the silicon, germanium, and tin compounds, respectively. (It should be remembered that while these differences are apparently significantly larger than the standard deviations, individually they may be considerably in error since bond lengths have not been corrected for anisotropic motion.)

The angles between axial fluorine atoms are 170.5 (2), 173.6 (1), and 174.4 (1)° for the silicon, germanium, and tin compounds, respectively. These distortions from 180° are in the same direction but smaller than those previously observed in all other *cis*-tetrachlorotin(IV) complexes.[5–9] At first sight it would seem that even fluorine atoms are sterically somewhat more bulky than the nitrogen atoms in these complexes, despite their smaller van der Waals radius. However there is no recognizable trend as the central element becomes larger. It is probably meaningless to attempt analysis of the angles since, even as the atoms are moved further apart, the central atom to fluorine bonds in particular become more polar leading to greater electrostatic repulsions, while as a further complication, the separation of nitrogen atoms in bipyridyl complexes appears constrained to be around 2.5 ± 0.15 Å.[29–31]

In conclusion, these structures have failed to provide evidence for p_π–d_π bonding effects which, it has been proposed, could be important in determining preference for the cis or trans isomer among adducts of the group IVa tetrahalides. Two possibilities exist: due to the diffuseness of the appropriate d orbitals the π bonding is weak and does not produce any very significant differences in bond length or perhaps π bonding is equally strong to the fluorine atoms and to the delocalized system of the bipyridyl moiety, thereby nullifying any differences in M–F bond distances.

Acknowledgments.—This work has been supported by the National Research Council of Canada. A 1967 Science Scholarship is acknowledged with gratitude by A. R. F. The assistance of Dr. D. F. R. Gilson of McGill University is gratefully acknowledged.

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