Registry No. $[(C_6H_5)_3P]AuCl$, 14243-64-2; $(C_6H_5)_3P$, 603-35-0; $[(C_6H_5)_3P]_2AuCl\cdot{}^1/_2C_6H_6$, 49788-36-5.

Supplementary Material Available. Table VI, a listing of structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$7.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-805.

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Crystal Structures of Tetrakis(pentafluorophenyl)tin(IV) and Tetrakis(pentafluorophenyl)germanium(IV)

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The crystal structures of tetrakis(pentafluorophenyl)tin, $(C_6F_5)_4Sn$, and tetrakis(pentafluorophenyl)germanium, $(C_6F_5)_4Ge$, have been determined from three-dimensional single-crystal X-ray data collected by the θ-2θ scan technique on a computer automated diffractometer. Both compounds crystallize in the tetragonal space group $I4_1/a$ with $a = 17.738$ (11) Å, $c = 8.094$ (5) Å, $Z = 4$ for $(C_6F_5)_4Sn$ and $a = 17.277$ (13) Å, $c = 8.122$ (7) Å, $Z = 4$ for $(C_6F_5)_4Ge$. The structures were solved by Patterson and Fourier methods and have been refined by a full-matrix least-squares procedure to a conventional R factor of 0.089 for 1011 reflections in the case of $(C_6F_5)_4Sn$ and 0.077 for 1181 reflections for $(C_6F_5)_4Ge$. In each case the structures consist of discrete $(C_6F_5)_4M$ units with exact $\bar{4}$ crystallographic symmetry. The Sn–C and Ge–C lengths and the C–Sn–C and C–Ge–C valency angles are 2.126 (8) Å, 1.956 (4) Å, 105.5 (4)°, 105.0 (2)°, respectively. The angle between the pentafluorophenyl ring plane and the C–M–C valency angle plane is 53.2° and 51.9° for the tin and germanium compounds, respectively. The rotation of the entire molecule from the a axis is 41.9° in $(C_6F_5)_4Sn$ and 42.0° in $(C_6F_5)_4Ge$. The crystal packing differs from that in the corresponding phenyl derivatives, and the structures represent examples where close packing is not required for the retention of $\bar{4}$ symmetry.

Introduction

Recently there have been a number of reports on the structures[2-8] of tetraphenyl compounds of the group IVa elements. These derivatives of the type MA_4, where M is a group IVa element and A is an organic aryl group, form molecular lattices which allow study of their crystal packing using geometrical[2] as well as nonbonded energy analysis.[9] A study of the conformations and orientations of the MA_4 molecular units in the crystalline state[10] should be very useful in providing models for the structures of more complex derivatives. The crystal structure investigations of tetrakis(pentafluorophenyl)tin and tetrakis(pentafluorophenyl)germanium[11] were undertaken to compare the structure and packing with the corresponding tetraphenyl derivatives.

Experimental Section

Clear colorless needle crystals of the title compounds[12] were kindly provided by Dr. C. Tamborski of the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio. For each compound a crystal which gave sharp optical extinction under crossed polarizers was mounted along its needle axis. On the basis of oscillation and indexed Weissenberg photographs both crystals were found to belong to the tetragonal system and the observed absences $h + k + l = 2n + 1$, h, $(k) = 2n + 1$ for $hk0$, $l = 4n + 1$ for $00l$ uniquely determine the space group[13] as $I4_1/a$. The needle axis corresponds to the c axis. Accurate values of the unit cell parameters for each crystal were determined at ambient room temperature from a least-squares refinement of the angular settings of 12 carefully centered reflections on a Picker FACS-1 computer-controlled (PDP-8/L) diffractometer using Mo Kα radiation (λ 0.71069 Å).

Crystal Data for $(C_6F_5)_4Sn$: tetragonal; space group $I4_1/a$; $a = 17.738$ (11) Å; $c = 8.094$ (5) Å; $V = 2547$ Å^3; $Z = 4$; $d_m = 2.0$ g cm^{-3}; $d_c = 2.05$ g cm^{-3}; mol wt = 784.9; $F(000) = 1496$; μ(Mo Kα) = 11.9 cm^{-1}.

Crystal Data for $(C_6F_5)_4Ge$: tetragonal, space group $I4_1/a$; $a = 17.277$ (13) Å; $c = 8.122$ (7) Å; $V = 2424$ Å^3; $Z = 4$; $d_m = 2.0$ g cm^{-3}; $d_c = 2.03$ g cm^{-3}; mol wt = 740.8, $F(000) = 1424$, μ(Mo Kα) = 15.3 cm^{-1}. The experimental densities, d_m, were measured by flotation in an aqueous solution of potassium iodide.

Collection and Reduction of the Intensity Data. For both crystals an independent set of three-dimensional intensity data were collected on the diffractometer already mentioned; zirconium filtered Mo Kα radiation was used. The dimensions of the $(C_6F_5)_4Sn$ crystal were 0.10 × 0.14 × 0.40 mm and for $(C_6F_5)_4Ge$ 0.10 × 0.10 × 0.28 mm. All reflections out to 52.5° in 2θ for tetrakis(pentafluorophenyl)germanium and 52° for the tin derivative were collected using the θ-2θ scan mode. For each crystal a symmetrical scan range in 2θ was used from −1° to +1° of the Mo Kα peak with an allowance made for the Kα_1-Kα_2 separation. The scan rate was 1°/min. A stationary-counter, stationary-crystal background count was measured for 20 sec at each end of the scan. To minimize coincidence losses a brass attenuator was inserted automatically whenever the count rate of the diffracted beam exceeded about 10,000 counts/sec. During the data collection for each crystal the intensities of three standard reflections in different regions of reciprocal space were monitored after every 100 reflections. Their intensities showed only statistical variation which indicated little counter or crystal instability throughout the data collection.

Each net intensity, I, was corrected for Lorentz and polarization factors (Lp) but not for absorption to give the observed structure

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Table III. Positional[a] and Thermal Parameters[b] for $(C_6F_5)_4Sn$

Atom	x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Sn	0	0	0	34 (1)	34 (1)	144 (2)	0	0	0
C(1)	0.0709 (4)	−0.0637 (5)	0.1590 (9)	40 (3)	39 (4)	140 (15)	0 (3)	11 (6)	10 (6)
C(2)	0.0780 (5)	−0.1422 (5)	0.1530 (11)	40 (4)	50 (4)	170 (16)	−2 (3)	−0 (7)	22 (7)
C(3)	0.1237 (6)	−0.1802 (6)	0.2647 (14)	58 (4)	48 (4)	242 (21)	−2 (4)	25 (9)	37 (9)
C(4)	0.1615 (5)	−0.1424 (7)	0.3884 (12)	43 (4)	68 (6)	180 (18)	8 (4)	18 (7)	26 (9)
C(5)	0.1560 (6)	−0.0651 (7)	0.3956 (12)	44 (4)	74 (6)	171 (18)	3 (4)	1 (7)	−5 (9)
C(6)	0.1099 (5)	−0.0278 (6)	0.2837 (11)	47 (4)	50 (4)	170 (18)	7 (3)	10 (7)	−2 (7)
F(2)	0.0427 (3)	−0.1819 (3)	0.0374 (7)	65 (2)	37 (2)	326 (14)	−6 (2)	−35 (5)	1 (4)
F(3)	0.1294 (4)	−0.2566 (3)	0.2546 (9)	81 (3)	51 (2)	455 (17)	4 (2)	−20 (6)	68 (7)
F(4)	0.2045 (3)	−0.1795 (4)	0.4976 (8)	64 (3)	97 (4)	273 (12)	16 (2)	−31 (5)	67 (6)
F(5)	0.1927 (3)	−0.0272 (4)	0.5152 (7)	74 (3)	101 (4)	224 (12)	13 (3)	−45 (5)	−33 (6)
F(6)	0.1056 (3)	0.0482 (3)	0.2956 (6)	73 (3)	55 (3)	267 (12)	11 (2)	−39 (4)	42 (4)

[a] The estimated standard deviations in the least significant figures are given in parentheses here and in other tables. [b] The thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Table IV. Positional and Thermal Parameters for $(C_6F_5)_4Ge$

Atom	x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Ge	0	0	0	32 (1)	32 (1)	120 (2)	0	0	0
C(1)	0.0668 (2)	−0.0601 (2)	0.1466 (5)	29 (1)	36 (2)	136 (8)	3 (1)	3 (3)	7 (3)
C(2)	0.0766 (2)	−0.1394 (3)	0.1415 (6)	34 (2)	41 (2)	158 (9)	−1 (1)	6 (3)	4 (3)
C(3)	0.1230 (3)	−0.1783 (3)	0.2524 (7)	40 (2)	46 (2)	216 (10)	2 (2)	8 (4)	34 (4)
C(4)	0.1600 (3)	−0.1387 (3)	0.3752 (6)	40 (2)	56 (3)	160 (9)	8 (2)	4 (4)	30 (4)
C(5)	0.1523 (3)	−0.0597 (3)	0.3854 (6)	38 (2)	63 (3)	128 (8)	1 (2)	−6 (3)	−4 (4)
C(6)	0.1061 (3)	−0.0220 (3)	0.2723 (6)	37 (2)	45 (2)	145 (8)	3 (2)	2 (3)	−2 (3)
F(2)	0.0412 (2)	−0.1818 (2)	0.0249 (4)	59 (1)	37 (1)	254 (6)	−4 (1)	−25 (2)	6 (2)
F(3)	0.1311 (2)	−0.2559 (2)	0.2412 (5)	70 (2)	43 (1)	371 (9)	4 (1)	−23 (3)	43 (3)
F(4)	0.2041 (2)	−0.1759 (2)	0.4860 (4)	61 (1)	85 (2)	234 (6)	16 (1)	−21 (3)	51 (3)
F(5)	0.1886 (2)	−0.0199 (2)	0.5048 (4)	61 (1)	84 (2)	193 (6)	5 (1)	−35 (3)	−23 (3)
F(6)	0.0997 (2)	0.0563 (2)	0.2846 (4)	61 (1)	48 (1)	219 (6)	6 (1)	−25 (2)	−29 (2)

factor amplitudes, F_o, using $I = C - (t_c/2t_B)(B_1 + B_2)$ and $F_o = (I/Lp)^{1/2}$. The estimated standard deviation in I, $\sigma(I)$, and in F_o, $\sigma(F_o)$, was computed from $\sigma(I) = [C + (t_c/2t_B)^2(B_1 + B_2) + (pI)^2]^{1/2}$ and $\sigma(F_o) = (2F_o)^{-1}(Lp)^{-1}\sigma(I)$. In these expressions C is the total count accumulated during the scan in time t_c, B_1 and B_2 are the background counts observed at each extreme of the scan each in a time t_B, and p[14] was taken to be 0.04. For $(C_6F_5)_4Sn$ a total of 1011 reflections and for $(C_6F_5)_4Ge$ a total of 1181 reflections have $I > \sigma(I)$ and were used in subsequent calculations.

Structure Determination and Refinement.[15] The structure solution for both compounds proceeded in a similar manner. In both cases there are four $M(C_6F_5)_4$ molecules per unit cell. The space group $I4_1/a$ has 16 general positions[13] which requires that the four metal atoms per unit cell be constrained at special positions with $\bar{4}$ symmetry. There is, therefore, only one pentafluorophenyl group in the asymmetric unit in each structure. Analysis of a three-dimensional Patterson synthesis was consistent with the placement of the heavy atoms at the origin. The six independent carbon atoms and five independent fluorine atoms were successfully found from a series of Fourier and difference Fourier maps which were phased by the atoms already located. The complete trial structure for each compound was refined assuming anisotropic thermal motion for all of the atoms by a full-matrix least-squares procedure. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where the weight, w, applied to each observation was taken to be $1/\sigma^2(F_o)$. A total of 102 parameters including one scale factor were varied in each case. The structure refinement converged to a conventional R_1 index, $\Sigma||F_o| - |F_c||/\Sigma|F_o|$, of 0.089 and a weighted R_2 index, $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$, of 0.064 for tetrakis(pentafluorophenyl)tin. For the germanium compound the final refined values of R_1 and R_2 were 0.077 and 0.063, respectively. For both compounds in the last cycle of least-squares refinement the largest shift in any positional and thermal parameter was 0.03 times its own standard deviation. The standard deviation in an observation of unit weight was 1.54 for $(C_6F_5)_4Sn$ and 1.51 for $(C_6F_5)_4Ge$. An analysis of $w(|F_o| - |F_c|)^2$ as a function of $|F_o|$ or $\sin\theta/\lambda$ showed no unusual trends. The neutral scattering factors for all atoms were taken from Cromer and Waber.[16] The scattering factors of Sn and Ge were corrected for the real and imaginary anomalous dispersion corrections given by Cromer.[17]

A final difference Fourier synthesis revealed no residual electron density maximum greater than 1 electron/Å^3 for both the germanium and tin derivatives and in each case these electron density peaks occurred within 0.9 Å of the respective heavy atom. The final observed and calculated structure factors are listed as $10|F_o|$ and $10|F_c|$ electrons for $(C_6F_5)_4Sn$ in Table I and for $(C_6F_5)_4Ge$ in Table II. (See paragraph at end of paper regarding supplementary material.) Final positional and thermal parameters for tetrakis(pentafluorophenyl)tin are presented in Table III and for the germanium compound in Table IV.

Description and Discussion of the Structure

Tetrakis(pentafluorophenyl)tin and tetrakis(pentafluorophenyl)germanium each have exact $\bar{4}$ symmetry in the crystalline state. Their structures consist of discrete $(C_6F_5)_4M$ molecular units linked together by a network of van der Waals interactions. Two views of the molecular structure and the atom numbering scheme are presented in Figures 1 and 2. The projection of the unit cell on the *ab* plane is shown in Figure 3. Interatomic distances and angles for both structures are given in Tables V and VI. The observed Ge-C(1) bond length is 1.957 (4) Å which compares with 1.957 (5) and 1.954 (1) Å found in $(C_6H_5)_4Ge$,[2,3] 1.956 (4) Å in $((C_6H_5)_2Ge)_2Fe_2(CO)_7$,[18] 1.945 (8) Å in $(C_6H_5)_3Ge(OCCH_3)$,[19] and 1.967 (8) Å in $(C_6H_5)_3GeCo_3(CO)_{11}$.[20] For the corresponding tin compound the refined Sn-C(1) length is 2.126 (8) Å and this compares with 2.14 (1) Å observed in

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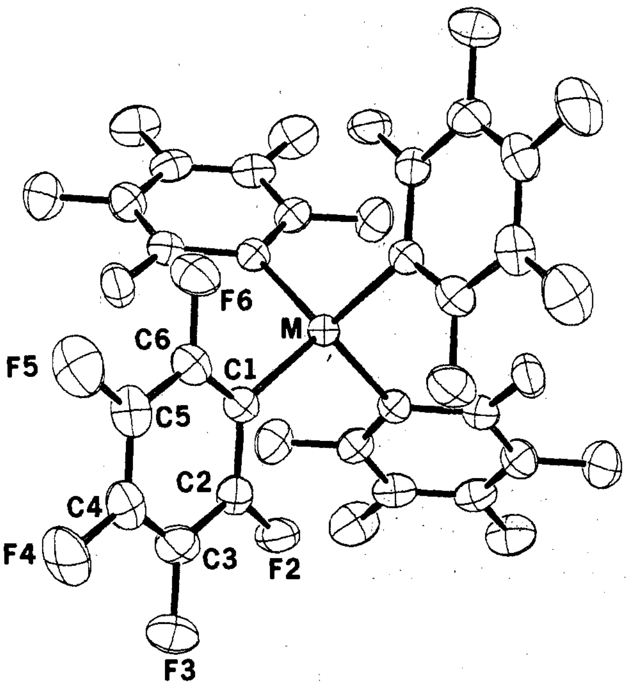

Figure 1. Labeling of atoms in $(C_6F_5)_4Sn$ and $(C_6F_5)_4Ge$. Because the structures of the tin and germanium compounds are so similar only the $(C_6F_5)_4Sn$ molecule is shown. This view is along the molecular $\bar{4}$ axis.

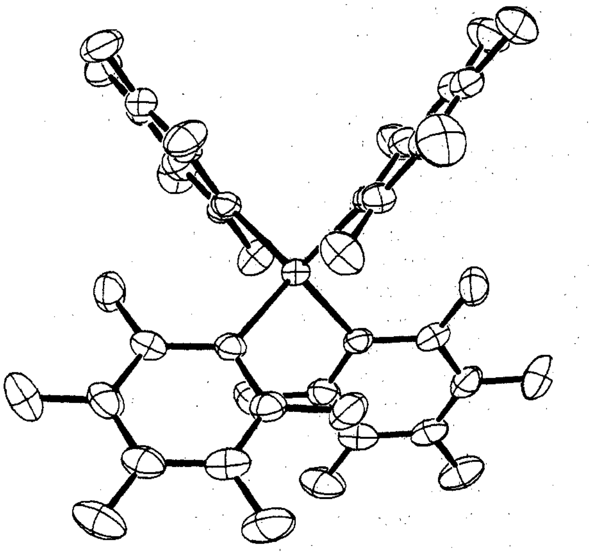

Figure 2. A view perpendicular to the molecular $\bar{4}$ axis of $(C_6F_5)_4Sn$.

$(C_6H_5)_4Sn$,[5,6] 2.13 Å in $(C_6H_5)_3SnFe(CO)_2\pi\text{-}C_5H_5$,[21] and 2.15 (1) Å in $(C_6H_5)_3SnMn(CO)_5$.[22] For Sn-alkyl bond lengths electron diffraction studies have yielded results of 2.134 (7) Å in $(CH_3)_4Sn$,[23] 2.150 (3) Å in $(CH_3)_2SnH_2$,[24] 2.147 (4) Å in $(CH_3)_3SnH$,[24] 2.106 (6) Å in $(CH_3)_3SnCl$,[24] and 2.108 (7) Å in $(CH_3)_2SnCl_2$.[23] The only reported X-ray crystal structure of a compound containing a tin-alkyl linkage and involving four-coordinate tin is the cyclohexyl derivative, $(C_6H_{11})_3Sn(O_2CCH_3)$,[25] where a mean Sn-C distance of 2.19 (3) Å was found. No structural results for Ge-alkyl bonded compounds seem to have been reported. For the analogous silicon derivatives the Si-C lengths are: 1.872 (7) Å in (C_6-

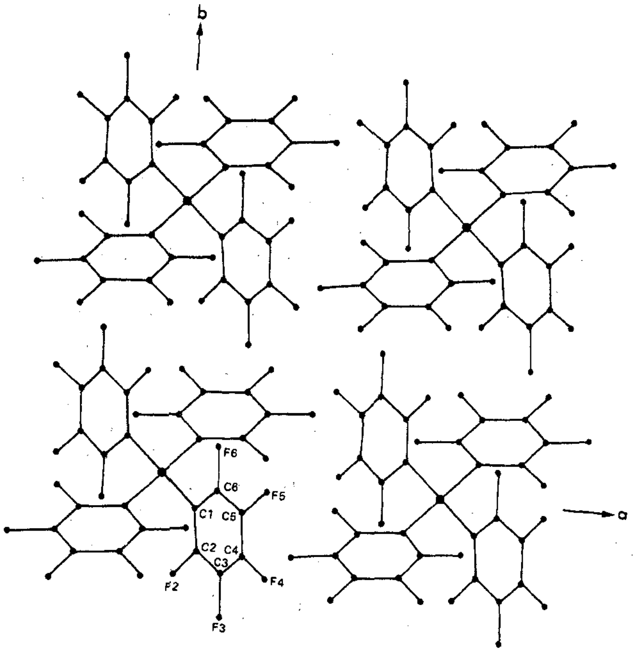

Figure 3. A projection on the *ab* plane of the $(C_6F_5)_4Ge$ unit cell. The $(C_6F_5)_4Sn$ unit cell is similar.

Table V. Interatomic Distances and Angles for $(C_6F_5)_4Sn$

Distances, Å			
C(1)-C(2)	1.398 (11)	C(2)-F(2)	1.328 (9)
C(2)-C(3)	1.389 (12)	C(3)-F(3)	1.362 (10)
C(3)-C(4)	1.379 (12)	C(4)-F(4)	1.340 (10)
C(4)-C(5)	1.376 (12)	C(5)-F(5)	1.347 (10)
C(5)-C(6)	1.388 (12)	C(6)-F(6)	1.355 (10)
C(6)-C(1)	1.379 (11)	Sn-C(1)	2.126 (8)
Angles, deg			
C(1)-C(2)-C(3)	120.8 (9)	F(2)-C(2)-C(1)	120.7 (8)
C(2)-C(3)-C(4)	121.5 (9)	F(2)-C(2)-C(3)	118.5 (9)
C(3)-C(4)-C(5)	118.7 (9)	F(3)-C(3)-C(2)	119.2 (10)
C(4)-C(5)-C(6)	119.3 (10)	F(3)-C(3)-C(4)	119.3 (10)
C(5)-C(6)-C(1)	123.6 (9)	F(4)-C(4)-C(3)	121.2 (10)
C(6)-C(1)-C(2)	116.1 (8)	F(4)-C(4)-C(5)	120.1 (11)
Sn-C(1)-C(2)	124.1 (4)	F(5)-C(5)-C(4)	119.6 (10)
Sn-C(1)-C(6)	119.6 (4)	F(5)-C(5)-C(6)	121.1 (10)
C(1)-Sn-C(1)$(\bar{x}\bar{y}z)$	105.5 (4)	F(6)-C(6)-C(5)	117.4 (9)
C(1)-Sn-C(1)$(\bar{y}x\bar{z})$	111.5 (2)	F(6)-C(6)-C(1)	119.0 (8)

Table VI. Interatomic Distances and Angles for $(C_6F_5)_4Ge$

Distances, Å			
C(1)-C(2)	1.382 (6)	C(2)-F(2)	1.344 (5)
C(2)-C(3)	1.380 (6)	C(3)-F(3)	1.352 (6)
C(3)-C(4)	1.367 (7)	C(4)-F(4)	1.343 (5)
C(4)-C(5)	1.374 (7)	C(5)-F(5)	1.345 (6)
C(5)-C(6)	1.380 (6)	C(6)-F(6)	1.360 (6)
C(6)-C(1)	1.392 (6)	Ge-C(1)	1.957 (4)
Angles, deg			
C(1)-C(2)-C(3)	122.2 (5)	F(2)-C(2)-C(1)	120.4 (4)
C(2)-C(3)-C(4)	120.3 (5)	F(2)-C(2)-C(3)	117.4 (4)
C(3)-C(4)-C(5)	119.7 (4)	F(3)-C(3)-C(2)	119.9 (5)
C(4)-C(5)-C(6)	119.0 (5)	F(3)-C(3)-C(4)	119.8 (5)
C(5)-C(6)-C(1)	123.1 (5)	F(4)-C(4)-C(3)	121.0 (5)
C(6)-C(1)-C(2)	115.6 (4)	F(4)-C(4)-C(5)	119.3 (5)
Ge-C(1)-C(2)	125.5 (2)	F(5)-C(5)-C(4)	120.4 (5)
Ge-C(1)-C(6)	118.9 (2)	F(5)-C(5)-C(6)	120.6 (5)
C(1)-Ge-C(1)$(\bar{x}\bar{y}z)$	105.0 (2)	F(6)-C(6)-C(5)	117.9 (4)
C(1)-Ge-C(1)$(\bar{y}x\bar{z})$	111.7 (1)	F(6)-C(6)-C(1)	119.0 (4)

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$H_5)_4Si$,[4] 1.89 (2) Å in $(CH_3)_4Si$,[26] and 1.876 Å in $(CH_3)_{10}Si_4N_2$.[27] At the usually accepted level of significance of 3σ there appears to be little difference between M-aryl and M-alkyl bond lengths for the main group elements silicon, germanium, and tin, although a small decrease (*ca.* 0.04 Å) might be expected due to the difference between carbon sp^2 and sp^3 radii. Any further shortening due to p_π-d_π bonding appears negligible. The opposite situation with transition metal aryl and alkyl bond lengths has been thoroughly discussed by Churchill.[28,29]

The pentafluorophenyl rings in both the germanium and tin derivatives are planar within experimental error but deviate substantially from ideal D_{6h} symmetry. Thus, the sum of the six interior C-C-C angles is 720.0° in both compounds, although the individual C-C-C angles vary from 116.1 (8)° to 123.6 (9)° in $(C_6F_5)_4Sn$ and 115.6 (4)° to 123.1 (5)° in $(C_6F_5)_4Ge$. For both compounds the C-C-C angle at the metal bonded carbon is substantially the smaller angle. This spread has been generally the case for previously determined structures containing C_6F_5 groups.[30,31] The least-squares planes of the rings and deviations of the individual atoms from the planes are given in Table VII. In each case the 11 ring atoms define a plane from which the atoms deviate only slightly. The tin and germanium atoms lie 0.09 and 0.08 Å from their respective pentafluorophenyl ring plane.

The mean carbon-carbon and carbon-fluorine lengths in $(C_6F_5)_4Sn$ are 1.385 ± 0.008 and 1.346 ± 0.013 Å. The corresponding average distances in $(C_6F_5)_4Ge$ are 1.379 ± 0.008 and 1.349 ± 0.007 Å. The variation in individual lengths (Tables V and VI) as well as the mean bond lengths compare quite favorably with those reported previously for pentafluorophenyl groups.[30,31] However, it is worth noting that the mean C-C bond distances are significantly less than the C-C length, 1.394 (7) Å, reported in hexafluorobenzene;[32] however, the mean C-F bond distances in the pentafluorophenyl derivatives are greater than the 1.327 (7) Å found in C_6F_6.[32]

Because of the rigid nature of the aryl group these structures may be conveniently described in terms of three angular parameters, which specify the orientation and conformation of the $(C_6F_5)_4M$ molecule in the unit cell. These angles follow. ϕ is the angle between the projection of the M-C(1) bond on the *ab* plane and the *a* axis. This angle defines the rotation of the molecule about the *c* axis. α is the angle between the pentafluorophenyl ring plane and the C(1)$(\bar{x},\bar{y},z)$-M-C(1) plane. The latter plane is fixed in these structures since the molecular $\bar{4}$ axis of the $(C_6F_5)_4M$ coincides with the crystal *c* axis. A clockwise rotation is taken as positive looking from the pentafluorophenyl ring to the central atom. The angle α defines the rotation of the aryl ring about the M-C(1) bond. θ is the C(1)$(\bar{x},\bar{y},z)$-M-C(1) valency angle.

For $(C_6F_5)_4Sn$ the ϕ, α, and θ angles are 41.9, 53.2, and 105.5°, respectively, while the corresponding angles in $(C_6F_5)_4Ge$ are 42.0, 51.9, and 105.0°, respectively. The tetraphenyl derivatives of tin and germanium may be described in a completely anaologous manner.[2] The comparison of the tetraphenyl and tetrakis(pentafluorophenyl) compounds is presented in Table VIII. The C(1)$(\bar{x},\bar{y},z)$-M-C(1) valency angle (θ angle) is smaller by about 4° in the pentafluorophenyl derivatives. This observed distortion indicates a significant elongation along the $\bar{4}$ axis of the "tetrahedral" molecular units and is not generally anticipated for such tetracoordinate group IVa compounds.

Table VII. Molecular Planes[a] in $(C_6F_5)_4Sn$ and $(C_6F_5)_4Ge$

Atom	Deviation from plane, Å	Atom	Deviation from plane, Å
Pentafluorophenyl Ring in $(C_6F_5)_4Sn$			
Plane: $0.7861X + 0.0982Y - 0.6102Z = 0.0932$			
C(1)	−0.000	F(2)	+0.000
C(2)	−0.009	F(3)	+0.007
C(3)	+0.010	F(4)	−0.011
C(4)	−0.007	F(5)	+0.002
C(5)	+0.015	F(6)	+0.003
C(6)	−0.011	Sn[b]	−0.093
Pentafluorophenyl Ring in $(C_6F_5)_4Ge$			
Plane: $0.7918X + 0.1174Y - 0.5994Z = 0.0829$			
C(1)	−0.005	F(2)	−0.009
C(2)	−0.006	F(3)	+0.017
C(3)	+0.010	F(4)	−0.013
C(4)	−0.003	F(5)	−0.001
C(5)	+0.002	F(6)	+0.010
C(6)	−0.001	Ge[b]	−0.083

[a] The planes are defined in cartesian coordinates where $X = xa$, $Y = yb$, $Z = zc$. [b] These atoms were given zero weight in the calculation of the least-squares plane. All other atoms were given unit weight.

The rotation of the aryl ring about the M-C(1) bond (α angle) is surprisingly similar in both series of compounds considering the range of possible conformations. This fact indicates that the intramolecular interactions between the aryl rings are quite comparable in both the phenyl and pentafluorophenyl derivatives. The difference in the crystal structures and packing must then involve the variation of the intermolecular contacts as a function of the particular aryl group. This conclusion is supported by noting that the ϕ angles which are largely determined by the intermolecular contacts[9] are completely different (see Table VIII) in the two series of compounds.

The value of α in tetraphenylsilicon and tetraphenyllead is 52.4 and 58.9°, respectively. The rather small observed range (52 to 59°) of the angle α in all the group IVa tetraphenyl derivatives and in the pentafluorophenyl compounds suggests the relative insensitivity of the conformation angle with respect to central atom size or type of aryl group. While more work is needed to support this contention, this idea has been used successfully in the determination of the structure of other similar compounds.[33]

A study[10] by Kitaigorodskii on the packing of MA_4 type compounds has been done. Kitaigorodskii proposed on the basis of symmetry arguments that those molecules which retain $\bar{4}$ symmetry in the solid state will crystallize in space groups $I\bar{4}$, $P4_2/n$, or $P\bar{4}2_1c$. These three space groups allow close packing of the MA_4 molecules and Kitaigorodskii has discussed the unsuitability[10] of other tetragonal space groups.

Kitaigorodskii's ideas[10] are supported with the phenyl and other derivatives of the group IVa elements. Thus, tetraphenylgermanium and tetraphenyltin crystallize in the noncentrosymmetric space group $P\bar{4}2_1c$ and the germanium and tin atoms are at $\bar{4}$ sites. The same is true for the other group

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Table VIII. Rigid Group Angular Parameters

Compd	ϕ, deg	α, deg	θ, deg
$(C_6H_5)_4Sn^{a,f}$	7.1	56.5	109.1
$(C_6H_5)_4Sn^{b,f}$	7.7	58.6	110.8
$(C_6F_5)_4Sn^{c,g}$	41.9	53.2	105.5
$(C_6H_5)_4Ge^{d,f}$	7.2	54.2	109.0
$(C_6F_5)_4Ge^{e,g}$	42.0	51.9	105.0

[a] See ref 5. [b] See ref 6. [c] This work. [d] See ref 2. [e] See ref 3; the value of α is incorrectly given in ref 8. [f] Space group $P\bar{4}2_1c$. [g] Space group $I4_1/a$.

IVa tetraphenyl compounds. In tetra(*p*-tolyl)tin[33,34] and tetra(*p*-methoxyphenyl)tin[35] the space group is $I\bar{4}$ and in each case the molecular symmetry is $\bar{4}$. On the other hand, in the pentafluorophenyl structures the tin and germanium atoms retain $\bar{4}$ symmetry in the crystal, but the space group is the centrosymmetric $I4_1/a$. In this space group close packing of molecules is not favored because adjacent molecules are related by mirror planes.[10] It is apparent that close packing is not a sufficient criterion for the retention of the highest molecular symmetry ($\bar{4}$) possible in the solid state.

The shortest intermolecular F· · ·F and F· · ·C nonbonded distances in $(C_6F_5)_4Sn$ are $F(4)\cdots F(4)(\bar{y}, -\frac{1}{2}+x, \frac{1}{4}+z)$, 2.919 Å, and $F(3)\cdots C(3)(\bar{y}, -\frac{1}{2}+x, \frac{1}{4}+z)$, 3.123 Å. For $(C_6F_5)_4Ge$ the corresponding distances are 2.943 and 3.089 Å for the same atom-atom contacts. The shortest intramolecular nonbonded distances are 3.018 Å in $(C_6F_5)_4Sn$ and 2.899 Å in $(C_6F_5)_4Ge$ for the $F(2)\cdots F(6)(y, \bar{x}, z)$ contact. From these distances a value of 1.46 Å is obtained for the van der Waals radius of fluorine which is consistent with that tabulated (1.47 Å) by Bondi.[36] The use of 1.46 Å for the fluorine van der Waals radius and the above C· · ·F contact distances leads to a van der Waals radius of 1.65 Å for carbon. This is about 0.1 Å less than the values given by Bondi[36] for an aromatic carbon.

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Supplementary Material Available. A listing of structure factor amplitudes (Tables I and II) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-811.

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Synthesis and Molecular Structure of Bis(6-mercapto-9-benzylpurine)palladium(II)-Dimethylacetamide

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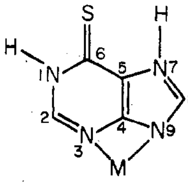
The compound bis(6-mercapto-9-benzylpurine)palladium(II)-dimethylacetamide, $C_{28}H_{27}N_9OS_2Pd$, was synthesized by allowing palladium(II) chloride to react with 6-mercapto-9-benzylpurine in dimethylacetamide, followed by the diffusion of 1-propanol vapors into the reaction solution. The crystals formed are monoclinic and belong to the space group *C*2/*c* with eight molecules per unit cell of dimensions $a = 24.80$ (1) Å, $b = 11.95$ (1) Å, $c = 22.03$ (1) Å, and $\beta = 114.73$ (5)°. The structure was solved by conventional heavy-atom methods using data collected on an automated four-circle diffractometer. The structure was refined on F to $R_1 = 0.076$ and $R_2 = 0.069$. The two phenyl groups were refined as rigid bodies. Both purine ligands are coordinated to palladium through the sulfur and N(7) atoms to form a five-membered chelate ring. The coordination geometry is a slightly distorted square with angles S1-Pd-S2 = 85.8 (1)° and N7A-Pd-N7B = 98.3 (4)°. The dimethylacetamide molecule is not coordinated. The presence of the metal atom does not influence the general tendency for purine rings to stack in a solid lattice, and stacking of this kind is a major intermolecular feature of the structure.

Introduction

6-Mercaptopurine was first synthesized by Hitchings[2] as a purine antimetabolite, with possible carcinostatic activity. A number of transition metal complexes[3] of this compound have been investigated as possible antitumor agents.[4] The reported complexes are amorphous, hydrated materials and are insoluble in organic solvents. The chief means of characterization of these complexes has been chemical analysis.

Grinberg[3b] proposed two types of metal attachment to the 6-mercaptopurine anion in these complexes. In the first type of attachment, the metal forms a four-membered chelate ring with atoms N3 and N9 (see **1**). Coordination



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