SHORT COMMUNICATIONS

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The crystal structures of the tetra(2-thienyl) derivatives of germanium, tin and lead. By A. KARIPIDES, A. T. REED, D. A. HALLER and F. HAYES, *Department of Chemistry, Miami University, Oxford, Ohio* 45056, *USA*

The crystal structures of the tetra(2-thienyl) derivatives of Ge, Sn and Pb have been determined from three-dimensional single-crystal X-ray diffraction data. All three compounds crystallize in space group $P\bar{4}2_1c$ and have crystallographically imposed $\bar{4}$ symmetry. The thienyl rings in each structure exhibit twofold orientational disorder, and structure refinement by rigid-body full-matrix least-squares methods yielded conventional R values of 0·095, 0·069 and 0·055 for $(C_4H_3S)_4Ge$, $(C_4H_3S)_4Sn$ and $(C_4H_3S)_4Pb$ respectively.

In the course of our studies of the structural chemistry of aryl Group IV*a* compounds we have determined the crystal structures of the tetra(2-thienyl) derivatives of Ge, Sn and Pb. These were prepared following published procedures and in each instance recrystallized from absolute ethanol in the form of long glistening needles (Krause & Renwanz, 1927, 1932). For each substance, indexed Weissenberg photographs revealed tetragonal symmetry and systematic absences, h odd for $h00$, l odd for hhl, uniquely determined the space group to be $P\bar{4}2_1c$. The pertinent crystal data are given in Table 1. Experimental densities were determined by flotation in aqueous potassium iodide solutions.

For each crystal, three-dimensional X-ray data were collected and reduced to values of F_o and $\sigma(F_o)$ (assuming an 'uncertainty factor' $p = 0·04$) in the manner previously described (Karipides, Forman, Thomas & Reed, 1974). Absorption corrections were not applied. After initial attempts at structure solution utilizing heavy-atom methods, it became apparent that the thienyl rings in each compound were twofold disordered in a way similar to that found in tetra(2-thienyl)silane (Karipides, Reed & Thomas, 1974). Independent refinements of individual atom positions were not suc-

cessful. Accordingly, the determination of the structure and refinement for each compound followed the rigid-body least-squares procedure described for the corresponding Si compound (Karipides, Reed & Thomas, 1974). In the rigid-group refinement the orientation and origin of the two disordered thienyl rings (rings A and B) were allowed to vary and were defined by six parameters: x_c, y_c, z_c, the origin of the rigid group [which was taken at the corresponding C(1) position in each ring], and χ_1, χ_2, χ_3 (the three rigid-group orientation angles discussed by Scheringer, 1963). The central atoms (Ge, Sn and Pb) were allowed to refine anisotropically, but only an overall isotropic temperature factor was refined for

Table 2. *Final parameters from the rigid-group refinement*

For the appropriate compound, the Ge, Sn and Pb atoms are each at the origin (0,0,0). For each central element the anisotropic temperature factor is in the form $\exp[-\beta_{11}(h^2 + k^2) - \beta_{33}l^2]$. (In $P\bar{4}2_1c$, $\beta_{11} = \beta_{22}$; $\beta_{12} = \beta_{13} = \beta_{23} = 0$.) For rings A and B, the overall isotropic temperature factors are given. The angles χ_1, χ_2, χ_3 are in radians.

	$(C_4H_3S)_4Ge$	$(C_4H_3S)_4Sn$	$(C_4H_3S)_4Pb$
β_{11}	0·0041 (2)	0·0045 (1)	0·0055 (2)
β_{33}	0·0165 (5)	0·0166 (3)	0·0198 (4)
Ring A			
x_c	0·136 (1)	0·148 (1)	0·151 (3)
y_c	0·024 (2)	0·027 (2)	0·029 (5)
z_c	0·170 (4)	0·184 (4)	0·190 (10)
χ_1	−0·041 (13)	−0·053 (14)	−0·052 (35)
χ_2	−0·001 (10)	0·009 (10)	0·044 (27)
χ_3	0·009 (17)	−0·008 (17)	−0·021 (43)
B	5·3 (2)	5·5 (2)	6·2 (4)
Ring B			
x_c	0·142 (1)	0·153 (1)	0·154 (3)
y_c	0·010 (2)	0·011 (1)	0·011 (4)
z_c	0·165 (3)	0·181 (3)	0·188 (8)
χ_1	0·033 (8)	0·008 (8)	−0·004 (22)
χ_2	0·011 (13)	0·009 (12)	−0·001 (32)
χ_3	0·047 (12)	0·043 (11)	0·046 (30)
B	2·9 (1)	3·3 (1)	4·0 (3)

Table 1. *Crystal and structure-analysis data for tetra(2-thienyl)germanium, -tin and -lead*

All three compounds crystallize in space group $P\bar{4}2_1c$ with $Z = 2$.

	$(C_4H_3S)_4Ge$	$(C_4H_3S)_4Sn$	$(C_4H_3S)_4Pb$
a (Å)	11·46 (2)	11·78 (2)	11·805 (16)
c (Å)	6·53 (1)	6·54 (1)	6·537 (9)
[$\lambda(MoK\alpha) = 0·71069$ Å]			
V (Å³)	858	907	911
D_o (g cm⁻³)	1·57	1·65	1·97
D_c (g cm⁻³)	1·53	1·63	1·96
Crystal size (mm)	0·17 × 0·11 × 0·11	0·28 × 0·22 × 0·11	0·15 × 0·08 × 0·08
μ(Mo $K\alpha$) (cm⁻¹)	23·4	18·5	95·4
Number of independent data, $I > \sigma(I)$	473	522	443
R	0·095	0·069	0·055
R_w	0·075	0·066	0·078
Goodness of fit	1·78	2·00	2·10

Table 3. *Derived thienyl-ring atom parameters from the final rigid-group refinements* ($\times 10^4$)

	$(C_4H_3S)_4Ge$			$(C_4H_3S)_4Sn$			$(C_4H_3S)_4Pb$		
	x	y	z	x	y	z	x	y	z
C(1) (A)	1365	237	1702	1475	274	1836	1510	290	1904
C(2) (A)	1552	1093	3130	1652	1097	3282	1675	1083	3406
C(3) (A)	2642	965	4151	2701	954	4333	2712	921	4476
C(4) (A)	3257	16	3475	3296	27	3661	3312	9	3763
S (A)	2515	−723	1601	2584	−672	1754	2617	−652	1794
H(2) (A)	940	1787	3445	1062	1777	3591	1084	1756	3740
H(3) (A)	2949	1552	5328	2995	1515	5528	2995	1457	5713
H(4) (A)	4104	−236	4051	4111	−230	4257	4120	−259	4365
C(1) (B)	1418	97	1649	1528	110	1808	1545	107	1878
C(2) (B)	2389	−600	1488	2455	−592	1656	2462	−602	1735
C(3) (B)	3295	−253	2846	3342	−273	3017	3353	−290	3086
C(4) (B)	2994	698	4004	3070	659	4168	3093	650	4222
S (B)	1611	1170	3446	1737	1151	3599	1769	1153	3650
H(2) (B)	2456	−1330	448	2506	−1304	620	2502	−1322	712
H(3) (B)	4128	−689	2952	4142	−718	3130	4145	−743	3204
H(4) (B)	3558	1097	5127	3625	1035	5292	2653	1025	5337

each ring. In each case the structure was refined by full-matrix least-squares methods: the quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$, where the weight, w, was taken to be $1/\sigma^2(F_o)$. The final agreement indices $R = \Sigma \|F_o| - |F_c\|/ \Sigma |F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, are given in Table 1. The atomic scattering factors for all elements were taken from Cromer & Waber (1974); corrections for $\Delta f'$ and $\Delta f''$ for Ge, Sn, Pb and S were made (Cromer & Liberman, 1970). The results from the rigid-group refinement are presented in Tables 2 and 3.*

The results of the refinement are in agreement with the disordered model. The angles between ring A and ring B are $175\cdot4$, $175\cdot5$ and $174\cdot6°$ for $(C_4H_3S)_4Ge$, $(C_4H_3S)_4Sn$ and $(C_4H_3S)_4Pb$ respectively. The molecular symmetry of each compound in the solid state is S_4 and the crystal packing and molecular configurations are essentially identical to that found in tetra(2-thienyl)silane (Karipides, Reed & Thomas, 1974). In the following comparisons only the mean values for the A and B rings are given. The Ge–C, Sn–C and Pb–C bond lengths are $1\cdot94$ (1), $2\cdot15$ (1) and $2\cdot20$ (1) Å respectively, while the $C(1)-M-C(1)(\overline{xyz})$ valence angles are $111\cdot5$ (Ge), $112\cdot6$ (Sn) and $111\cdot6°$ (Pb). The conformation of the thienyl ring is independent of the central-atom size and is specified by the angle between the thienyl-ring plane and the valence-angle plane, $C(1)-M-C(1)(\overline{xyz})$. A clockwise rotation about the $M-C(1)$ bond measured for the valence-

angle plane is taken as positive looking from the thienyl ring to the central atom. For $(C_4H_3S)_4Ge$, $(C_4H_3S)_4Sn$ and $(C_4H_3S)_4Pb$, the conformation angles are $57\cdot8$, $58\cdot4$ and $58\cdot4°$ respectively. These tetra(2-thienyl) derivatives have molecular configurations and conformations similar to the corresponding tetraphenyl compounds, again suggesting that 2-thienyl and phenyl groups provide comparable intra- and intermolecular interactions (Karipides, Reed & Thomas, 1974).

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32239 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.