

## Structure and Solid-State Tin-119 and Tellurium-125 NMR Spectra of 2,2,4,4,6,6-Hexakis(trimethylsilylmethyl)cyclotristannatellurane

BY FREDERICK W. B. EINSTEIN,\* IAN D. GAY, COLIN H. W. JONES, ANDREAS RIESEN  
AND RAJENDRA D. SHARMA

Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S5

(Received 25 February 1992; accepted 4 August 1992)

**Abstract.**  $\{[(\text{CH}_3)_3\text{SiCH}_2]_2\text{SnTe}\}_3$ ,  $\text{C}_{24}\text{H}_{66}\text{Si}_6\text{Sn}_3\text{Te}_3$ ,  $M_r = 1262.2$ , monoclinic,  $P2_1/c$ ,  $a = 18.392(3)$ ,  $b = 12.7234(3)$ ,  $c = 22.183(3)$  Å,  $\beta = 107.86(2)^\circ$ ,  $V = 4941 \text{ \AA}^3$ ,  $Z = 4$ ,  $D_x = 1.698 \text{ g cm}^{-3}$ ,  $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$ ,  $\mu = 34.14 \text{ cm}^{-1}$ ,  $F(000) = 2399.8$ ,  $T = 293 \text{ K}$ ,  $R = 0.047$  for 2480 observed reflections. The molecule has a twist-boat conformation similar to that of  $[(\text{CH}_3)_3\text{SnTe}]_3$ . The solid-state  $^{119}\text{Sn}$  and  $^{125}\text{Te}$  NMR parameters are briefly discussed.

**Introduction.** The present work follows on from a detailed study of the  $^{119}\text{Sn}$  and  $^{125}\text{Te}$  solid-state NMR spectroscopy of  $[(\text{CH}_3)_3\text{SnTe}]_3$  (Gay, Jones & Sharma, 1989). The correlation of solid-state NMR parameters with X-ray structural data of the present compound is of particular interest because it crystallizes in a monoclinic form with three inequivalent Sn and Te atoms.

**Experimental.** The title compound was synthesized by reacting a solution of  $\text{NaHTe}$ , prepared by reducing Te with  $\text{NaBH}_4$  in ethanol under oxygen-free nitrogen, with a stoichiometric quantity of  $[(\text{CH}_3)_3\text{SiCH}_2]_2\text{SnCl}_2$ . The resulting solid was recrystallized from hexane as yellow–green needles. A crystal was mounted in a 0.2 mm glass capillary. Cell-parameter determination (25 reflections,  $14.9 \leq \theta \leq 16.9^\circ$ ) and data acquisition were performed using an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated  $\text{Mo } K\alpha$  radiation. Two standard intensities were measured every hour of acquisition time and showed a systematic loss of intensity of about 2%. The crystal diffracted weakly so that at  $\theta = 20^\circ$  a large fraction of the reflections were unobserved and therefore the data collection was stopped (see below). An analytical absorption correction (de Meulenaer & Tompa, 1965), with transmission factors ranging from 0.712 to 0.874, was made to the data. Data reduction, including scaling, Lorentz and polarization corrections, was then performed.

Table 1. Data acquisition and refinement details for  $\{[(\text{CH}_3)_3\text{SiCH}_2]_2\text{SnTe}\}_3$

|   |   |
|---|---|
| Crystal dimensions (mm)                       | 0.08 × 0.20 × 0.40  |
| Scan mode                                     | $\omega/2\theta$  |
| Scan speed ( $^\circ \text{ min}^{-1}$ )      | 0.6–2.4   |
| Scan width ( $^\circ$ )                       | $0.80 + 0.35 \tan \theta$   |
| Range $2\theta$ ( $^\circ$ )                  | 4–40  |
| Range of $hkl$                                | $-16 \leq h \leq 16$ , $0 \leq k \leq 12$ , $0 \leq l \leq 20$<br>(unique set only) |
| No. of unique measured reflections            | 4976  |
| No. of reflections with $I \geq 2.0\sigma(I)$ | 2480  |
| Refined parameters                            | 297   |
| $R$   | 0.047   |
| $wR^*$  | 0.061   |
| $S$   | 1.07  |

\* The weighting scheme  $w = [1.697t_0(X) + 1.977t_1(X) + 0.710t_2(X)]^{-1}$ , where  $X = |F_o|/F_{\text{max}}$  and  $t_n$  are the polynomial functions of the Chebyshev series (Carruthers & Watkin, 1979), proved satisfactory.

The coordinates for the Te and Sn atoms were determined by direct methods (Gabe, Larson, Lee & Le Page, 1984). All non-H atoms were located using difference Fourier maps. H atoms were fixed at calculated positions with two equivalent isotropic temperature-factor variables for the methylene  $[0.08(2) \text{ \AA}^2]$  and the methyl type  $[0.18(2) \text{ \AA}^2]$ . The final full-matrix least-squares refinement, minimizing  $\sum w(|F_o| - |F_c|)^2$ , included anisotropic thermal parameters for all non-H atoms except for the methylene C atoms which were kept isotropic. The refinement was terminated when the maximum shift/e.s.d. dropped below 0.02. The final difference map had the largest peak of  $1.1(3) \text{ e \AA}^{-3}$ ,  $1.34 \text{ \AA}$  from Sn(3). A summary of details of data acquisition and structure refinement is given in Table 1. Atomic scattering factors and  $f'$ ,  $f''$  values were obtained from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Data reduction and absorption corrections were made using the *NRCVAX* system (Gabe *et al.*, 1984). Refinement (on  $F$ ) of the initial model was carried out using the *CRYSTALS* system (Watkin, Carruthers & Betteridge, 1985). Fig. 1 was generated by *ORTEP* (Johnson, 1965). Computations were performed with a MicroVAX II computer. The final positional and thermal-motion parameters for the

\* To whom correspondence should be addressed.

non-H atoms are given in Table 2.\* Selected bond distances, bond angles and torsion angles are given in Table 3. The molecular structure is similar to that found for hexamethylcyclotristannatellurane (Batchelor, Einstein & Jones, 1989) – viz twist-boat conformation for the six-membered ring. The relatively low density is consistent with the high volume/non-H-atom ratio ( $34 \text{ \AA}^3$ ) and the rapid intensity drop-off (large thermal motion).

Solid-state NMR spectra were measured on the instrument previously described (Gay, Jones & Sharma, 1989). This gave resonance frequencies of 22.4 and 18.9 MHz for  $^{119}\text{Sn}$  and  $^{125}\text{Te}$ , respectively. Chemical shifts are reported relative to  $(\text{CH}_3)_4\text{Sn}$  and  $(\text{CH}_3)_2\text{Te}$ . Chemical-shift anisotropies were measured by least-squares fitting of side-band intensities to intensities calculated by the Herzfeld–Berger method (Herzfeld & Berger, 1980).

**Discussion.** In comparison with  $[(\text{CH}_3)_2\text{SnTe}]_3$ , which exists in both monoclinic and tetragonal forms,  $\{[(\text{CH}_3)_3\text{SiCH}_2]_2\text{SnTe}\}_3$  appears to occur in only a monoclinic form. The molecule again exists in a twist-boat conformation and the bond angles about Sn and Te atoms and the Sn—Te bond lengths are similar to those observed in  $[(\text{CH}_3)_2\text{SnTe}]_3$ . As in the monoclinic form of the methyl compound, the three Sn atoms and Te atoms are crystallographically

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55635 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1004]

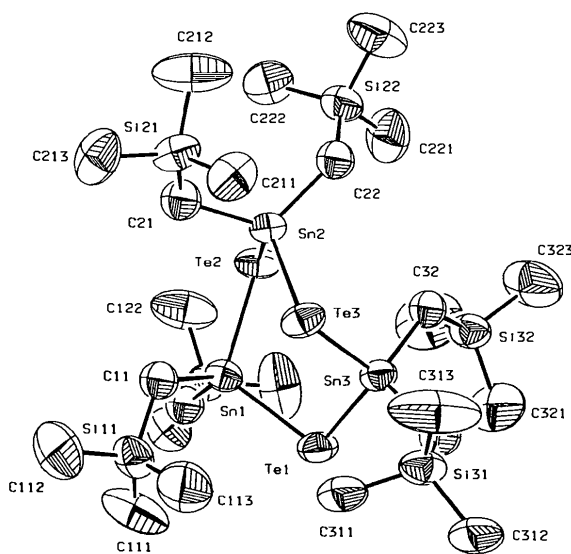


Fig. 1. Molecular structure of  $\{[(\text{CH}_3)_3\text{SiCH}_2]_2\text{SnTe}\}_3$  with 50% enclosure thermal ellipsoids; H atoms not shown.

Table 2. Fractional atomic coordinates ( $\times 10^4$ ) and isotropic or equivalent isotropic thermal parameters ( $\text{\AA}^2$ )

Methylene C atoms were refined isotropically. For the other atoms  $U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$ .

|        | x          | y         | z          | $U_{\text{iso}}/U_{\text{eq}}$ |
|--------|------------|-----------|------------|--------------------------------|
| Te(1)  | 1090.8 (9) | 3760 (2)  | 493.1 (9)  | 0.0779                         |
| Te(2)  | 3421.2 (9) | 5220 (2)  | 900.9 (9)  | 0.0717                         |
| Te(3)  | 3023.1 (9) | 2587 (2)  | 2145.0 (8) | 0.0720                         |
| Sn(1)  | 2001.3 (9) | 5407 (1)  | 1046.1 (8) | 0.0627                         |
| Sn(2)  | 4068.8 (8) | 3915 (1)  | 1902.2 (8) | 0.0612                         |
| Sn(3)  | 2160.5 (9) | 2216 (1)  | 922.4 (8)  | 0.0636                         |
| Si(11) | 1191 (5)   | 5640 (7)  | 2242 (4)   | 0.0864                         |
| Si(12) | 1593 (4)   | 7272 (6)  | -186 (4)   | 0.0801                         |
| Si(21) | 5182 (4)   | 4221 (7)  | 3453 (4)   | 0.0799                         |
| Si(22) | 5548 (4)   | 3520 (7)  | 1240 (4)   | 0.0859                         |
| Si(31) | 1276 (4)   | 283 (7)   | 1590 (4)   | 0.0807                         |
| Si(32) | 2480 (4)   | 1979 (7)  | -535 (4)   | 0.0812                         |
| C(11)  | 2101 (14)  | 5631 (20) | 2018 (12)  | 0.0767 (74)                    |
| C(12)  | 1458 (14)  | 6785 (21) | 545 (12)   | 0.0836 (80)                    |
| C(21)  | 4494 (15)  | 4844 (22) | 2755 (12)  | 0.0862 (80)                    |
| C(22)  | 4917 (14)  | 2955 (21) | 1685 (12)  | 0.0795 (77)                    |
| C(31)  | 1507 (16)  | 776 (22)  | 897 (13)   | 0.0927 (87)                    |
| C(32)  | 2901 (14)  | 2016 (20) | 347 (12)   | 0.0775 (76)                    |
| C(111) | 353 (13)   | 6176 (33) | 1640 (12)  | 0.1224                         |
| C(112) | 1356 (26)  | 6422 (42) | 2965 (18)  | 0.1717                         |
| C(113) | 931 (21)   | 4279 (13) | 2360 (18)  | 0.1388                         |
| C(121) | 860 (14)   | 8292 (19) | -471 (13)  | 0.1090                         |
| C(122) | 2549 (10)  | 7844 (28) | -26 (17)   | 0.1298                         |
| C(123) | 1490 (26)  | 6209 (19) | -763 (13)  | 0.1356                         |
| C(211) | 4963 (16)  | 2841 (12) | 3574 (14)  | 0.1023                         |
| C(212) | 6143 (10)  | 4257 (36) | 3369 (17)  | 0.1273                         |
| C(213) | 5197 (19)  | 4991 (22) | 4156 (10)  | 0.1104                         |
| C(221) | 5067 (18)  | 3399 (30) | 385 (6)    | 0.1252                         |
| C(222) | 5795 (16)  | 4904 (12) | 1448 (14)  | 0.1010                         |
| C(223) | 6432 (14)  | 2741 (28) | 1454 (18)  | 0.1414                         |
| C(311) | 981 (15)   | 1341 (18) | 2029 (14)  | 0.1054                         |
| C(312) | 477 (14)   | -640 (23) | 1288 (17)  | 0.1176                         |
| C(313) | 2093 (13)  | -387 (36) | 2144 (21)  | 0.1344                         |
| C(321) | 1504 (12)  | 1453 (35) | -793 (14)  | 0.1244                         |
| C(322) | 2501 (25)  | 3307 (17) | -852 (19)  | 0.1899                         |
| C(323) | 3079 (18)  | 1125 (31) | -853 (16)  | 0.1487                         |

Table 3. Selected bond distances ( $\text{\AA}$ ), bond angles ( $^\circ$ ) and torsion angles ( $^\circ$ )

|                         |            |                         |            |
|-------------------------|------------|-------------------------|------------|
| Te(1)—Sn(1)             | 2.726 (3)  | Sn(1)—C(11)             | 2.13 (2)   |
| Te(1)—Sn(3)             | 2.735 (3)  | Sn(1)—C(12)             | 2.15 (3)   |
| Te(2)—Sn(1)             | 2.740 (2)  | Sn(2)—C(21)             | 2.16 (3)   |
| Te(2)—Sn(2)             | 2.734 (2)  | Sn(2)—C(22)             | 2.15 (3)   |
| Te(3)—Sn(2)             | 2.734 (2)  | Sn(3)—C(31)             | 2.18 (3)   |
| Te(3)—Sn(3)             | 2.731 (2)  | Sn(3)—C(32)             | 2.15 (2)   |
| Sn(3)—Te(1)—Sn(1)       | 96.69 (7)  | C(21)—Sn(2)—Te(3)       | 104.6 (7)  |
| Sn(2)—Te(2)—Sn(1)       | 98.69 (7)  | C(22)—Sn(2)—Te(2)       | 109.1 (7)  |
| Sn(3)—Te(3)—Sn(2)       | 98.08 (7)  | C(22)—Sn(2)—Te(3)       | 107.3 (7)  |
| Te(2)—Sn(1)—Te(1)       | 110.92 (8) | C(31)—Sn(3)—Te(1)       | 105.1 (7)  |
| Te(3)—Sn(2)—Te(2)       | 112.11 (7) | C(31)—Sn(3)—Te(3)       | 108.5 (7)  |
| Te(3)—Sn(3)—Te(1)       | 111.04 (8) | C(32)—Sn(3)—Te(1)       | 113.5 (7)  |
| C(11)—Sn(1)—Te(1)       | 114.1 (7)  | C(32)—Sn(3)—Te(3)       | 109.2 (7)  |
| C(11)—Sn(1)—Te(2)       | 110.0 (7)  | C(12)—Sn(1)—C(11)       | 107.3 (10) |
| C(12)—Sn(1)—Te(1)       | 105.5 (7)  | C(22)—Sn(2)—C(21)       | 114.4 (9)  |
| C(12)—Sn(1)—Te(2)       | 108.6 (7)  | C(22)—Sn(3)—C(31)       | 109.3 (10) |
| C(21)—Sn(2)—Te(2)       | 109.3 (7)  | Sn(3)—Te(1)—Sn(1)—Te(2) | 43.4 (1)   |
| Sn(3)—Te(1)—Sn(1)—Te(2) | 43.4 (1)   | Te(1)—Sn(1)—Te(2)—Sn(2) | -83.8 (1)  |
| Sn(1)—Te(2)—Sn(2)—Te(3) | 31.5 (1)   | Te(2)—Sn(2)—Te(3)—Sn(3) | 37.2 (1)   |
| Sn(2)—Te(3)—Sn(3)—Te(1) | -84.6 (1)  | Te(2)—Sn(3)—Te(1)—Sn(1) | 39.9 (1)   |

inequivalent, although there is a pseudo-twofold axis through the molecule.

For  $[(\text{CH}_3)_2\text{SnTe}]_3$  it was not possible to prepare macroscopic quantities of the monoclinic form and the solid-state NMR study (Gay *et al.*, 1989, 1990) was carried out only on the tetragonal modification. The present compound presented an interesting case

Table 4. Observed isotropic shifts (p.p.m.) and couplings (Hz)

|       | $\delta^*$ | $^1J(^{119}\text{Sn}-^{125}\text{Te})$ |
|-------|------------|--|
| Te(a) | -713       | 3086, 3145                             |
| Te(b) | -781       | 3030, 3161                             |
| Te(c) | -817       | 3197, 3227                             |
| Sn(a) | -185       | 3150, 3238                             |
| Sn(b) | -183.4     | 3089, 3158                             |
| Sn(c) | -233.6     | 3043, 3190                             |

\* Shifts are with respect to (CH<sub>3</sub>)<sub>4</sub>Sn ( $\pm 0.3$  p.p.m.) or (CH<sub>3</sub>)<sub>2</sub>Te ( $\pm 1$  p.p.m.).

for study by solid-state NMR, given the presence of three inequivalent Sn and Te atoms.

The <sup>119</sup>Sn and <sup>125</sup>Te solid-state NMR spectra showed the presence of three Sn resonances and three Te resonances which, in each case, were clearly resolved. The <sup>119</sup>Sn and <sup>125</sup>Te isotropic shifts and <sup>1</sup>J(<sup>119</sup>Sn-<sup>125</sup>Te) coupling constants are given in Table 4. The <sup>2</sup>J(Sn-Sn) couplings were not resolved but all lie in the range 200–270 Hz. Similarly, the <sup>2</sup>J(Te-Te) couplings were not resolved but lie in the range 140–160 Hz. The magnitudes of the shifts and couplings observed here are similar to those in [(CH<sub>3</sub>)<sub>2</sub>SnTe]<sub>3</sub>(tetragonal).

From the Herzfeld-Berger chemical-shift anisotropy parameters listed in Table 5, it can be seen that Sn(c) has a shift tensor that is axially symmetric within the experimental e.s.d. Given the presence of a pseudo-twofold axis in the molecule it is possible that Sn(c) in the NMR data corresponds to Sn(c) in the crystal data.

Table 5. Herzfeld-Berger chemical-shift anisotropy parameters,  $\Delta\sigma$  (p.p.m.) and  $\rho$ 

|       | $\Delta\sigma$ | $\rho$           |
|-------|----------------|------------------|
| Te(a) | 407 $\pm$ 2    | -0.12 $\pm$ 0.03 |
| Te(b) | 634 $\pm$ 5    | -0.28 $\pm$ 0.02 |
| Te(c) | 602 $\pm$ 4    | -0.18 $\pm$ 0.02 |
| Sn(a) | 800 $\pm$ 16   | -0.79 $\pm$ 0.07 |
| Sn(b) | 792 $\pm$ 9    | 0.66 $\pm$ 0.03  |
| Sn(c) | 463 $\pm$ 7    | -0.98 $\pm$ 0.05 |

AR is grateful for a grant from the Swiss National Science Foundation. NSERC provided support for this work.

#### References

- BATCHELOR, R. J., EINSTEIN, F. W. B. & JONES, C. H. W. (1989). *Acta Cryst.* **C45**, 1813–1815.  
 CARRUTHERS, J. R. & WATKIN, D. J. (1979). *Acta Cryst.* **A35**, 698–699.  
 GABE, E. J., LARSON, A. C., LEE, F. L. & LE PAGE, Y. (1984). *NRCVAX Crystal Structure System*. National Research Council, Ottawa, Canada.  
 GAY, I. D., JONES, C. H. W. & SHARMA, R. D. (1989). *J. Magn. Reson.* **84**, 501–514.  
 GAY, I. D., JONES, C. H. W. & SHARMA, R. D. (1990). *J. Magn. Reson.* **89**, 657–658.  
 HERZFELD, J. & BERGER, A. (1980). *J. Chem. Phys.* **73**, 6021–6030.  
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.  
 MEAULENAER, J. DE & TOMPA, H. (1965). *Acta Cryst.* **19**, 1014–1018.  
 WATKIN, D. J., CARRUTHERS, J. R. & BETTERIDGE, P. W. (1985). *CRYSTALS*. Chemical Crystallography Laboratory, Univ. of Oxford, England.

*Acta Cryst.* (1993). **C49**, 472–475

## Structures of Bis(triphenylphosphine)gold(I) Hexafluorophosphate, [Au(PPh<sub>3</sub>)<sub>2</sub>]PF<sub>6</sub> (1), and Bis(triphenylphosphine)gold(I) Nitrate, [Au(PPh<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub> (2)

BY RICHARD J. STAPLES, CHRISTOPHER KING, MOHAMED N. I. KHAN, RICHARD E. P. WINPENNY AND JOHN P. FACKLER JR\*

Department of Chemistry, Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, TX 77843–3255, USA

(Received 21 January 1992; accepted 11 August 1992)

**Abstract.** [Au(C<sub>18</sub>H<sub>15</sub>P)<sub>2</sub>]PF<sub>6</sub> (1),  $M_r = 866.5$ , monoclinic,  $P2_1/c$ ,  $a = 9.927$  (1) Å,  $b = 20.086$  (5) Å,  $c = 17.500$  (5) Å,  $\beta = 96.72$  (1)°,  $V = 3465$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.66$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 44.28$  cm<sup>-1</sup>,  $F(000) = 1696$ ,  $T = 295$  K, final  $R = 0.0372$ ,  $wR = 0.0380$  for 2818 observed reflections [ $F_o^2 > 3\sigma(F_o^2)$ ]. [Au(C<sub>18</sub>H<sub>15</sub>P)<sub>2</sub>]NO<sub>3</sub> (2),  $M_r = 783.5$ ,

monoclinic,  $P2_1/n$ ,  $a = 17.502$  (5) Å,  $b = 11.020$  (1) Å,  $c = 18.012$  (3) Å,  $\beta = 112.40$  (2)°,  $V = 3212$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.62$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 47.04$  cm<sup>-1</sup>,  $F(000) = 1544$ ,  $T = 295$  K, final  $R = 0.0331$ ,  $wR = 0.0380$  for 3540 observed reflections. The coordination at the Au<sup>I</sup> centres is essentially linear with P—Au—P bond angles of 177.4 (1)° in (1) and 171.1 (2), 168.4 (1)° in (2). The nitrate anion in complex (2) does not interact with the Au<sup>I</sup> center.

\* To whom correspondence should be addressed.