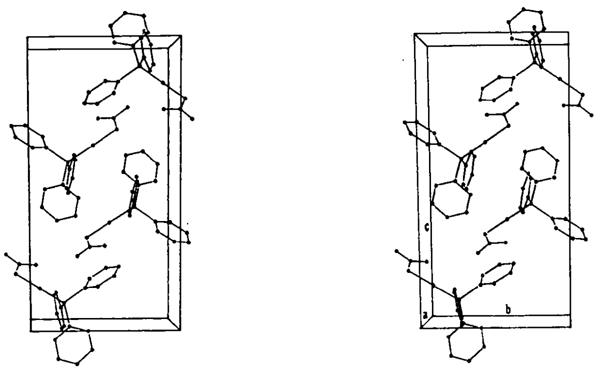

Fig. 2. A stereoview packing diagram viewed down the *a* axis.

The coordination of Au is essentially linear with O(1)—Au—P = 179·2 (2)°. The Au—P bond distance, 2·208 (3) Å, is short compared to other AuPPh$_3X$ compounds (Jones, 1984, and references therein). However, this short distance is quite common in Au$^{\rm I}$ compounds with oxygen *trans* to the Au—P bond (Jones, 1984, 1985; Hohbein, Jones, Meyer-Base, Schwarzmann & Sheldrick, 1985; Jones & Schelbach, 1988).

The nitrate is covalently bonded to gold through one oxygen atom. The Au—O(1) bond distance, 2·074 (8) Å, is comparable to other Au$^{\rm I}$—oxygen bond distances in AuPPh$_3X$ compounds. The distortion of the Au—O(1)—N angle [115·4 (7)°] from trigonal is small but significant. The Au···O(3) [2·84 (1) Å] and Au···N [2·84 (1) Å] distances are short but nonbonding. The monodentate coordination mode of Au to the nitrate ligand in the present compound [one bonding interaction, Au—O(1), and two nonbonding interactions, Au···O(3) and Au···N] is different from that observed in the metal cluster compound [AuIr$_3$(NO$_3$)(dppe)$_3$]BF$_4$ (Casalnuovo, Pignolet, van der Velden, Bour & Steggerda, 1983), wherein the nitrate ligand chelates to the gold with two long Au—O distances (2·36, 2·55 Å).

These studies have been supported by the National Science Foundation NSF-8708625, the Welch Foundation, and the Texas A&M University Center for Energy and Mineral Resources.

### References

Barron, P. F., Engelhardt, L. M., Healy, P. C., Oddy, J. & White, A. H. (1987). *Aust. J. Chem.* **40**, 1545–1555.

Casalnuovo, A. L., Pignolet, L. H., van der Velden, J. W. A., Bour, J. J. & Steggerda, J. J. (1983). *J. Am. Chem. Soc.* **105**, 5957–5958.

Heinrich, D. D., Khan, M. N. I., Fackler, J. P. Jr & Porter, L. C. (1988). *Inorg. Chem.* Submitted.

Hohbein, R., Jones, P. G., Meyer-Base, K., Schwarmann, E. & Sheldrick, G. M. (1985). *Z. Naturforsch. Teil B*, **40**, 1029–1031.

*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Jones, P. G. (1984). *Acta Cryst.* C**40**, 1320–1322.

Jones, P. G. (1985). *Acta Cryst.* C**41**, 905–906.

Jones, P. G. & Schelbach, R. (1988). *J. Chem. Soc. Chem. Commun.* p. 1338.

Khan, M. N. I., Wang, S., Heinrich, D. D. & Fackler, J. P. Jr. (1988). *Acta Cryst.* C**44**, 822–825.

Sheldrick, G. M. (1986). *SHELXTL. An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data.* Nicolet XRD Corp., Madison, WI, USA.

Steggerda, J. J., Bour, J. J. & van der Welden, J. W. A. (1982). *Recl Trav. Chim. Pays-Bas*, **101**, 164–170.

---

*Acta Cryst.* (1989). C**45**, 1010–1012

# Structure of Tetramethyltin, Sn(CH$_3$)$_4$

By Bernt Krebs,* Gerald Henkel and Mechtild Dartmann

*Anorganisch-Chemisches Institut der Universität Münster, Wilhelm-Klemm-Strasse* 8, *D*-4400 *Münster, Federal Republic of Germany*

(*Received* 22 *November* 1988; *accepted* 3 *January* 1989)

**Abstract.** [Sn(CH$_3$)$_4$], $M_r = 178{\cdot}84$, cubic, $Pa3$, $a = 11{\cdot}198\,(3)$ Å, $V = 1404{\cdot}2$ Å$^3$, $Z = 8$, $D_x = 1{\cdot}69$ Mg m$^{-3}$, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu(\mathrm{Mo}\,K\alpha) = 3{\cdot}54$ mm$^{-1}$, $F(000) = 688$, $T = 158$ K, $R = 0{\cdot}050$, $wR = 0{\cdot}058$ for 505 unique observed reflections [$I > 1{\cdot}96\sigma(I)$]. The compound crystallizes in the SnI$_4$ structure type with the tetrahedral molecule on a threefold axis with three equivalent Sn—C bond lengths of 2·138 (6) Å, and the fourth of 2·102 (8) Å. No significant angular distortion is observed. The slight nonequivalence of the bond lengths is in accordance with inelastic neutron scattering and NMR data.

**Introduction.** The molecular structures of the tetramethyl derivatives of the heavy elements of the fourth main group are well documented. Electron diffraction

---

* To whom correspondence should be addressed.

Table 1. *Atomic coordinates of all atoms and anisotropic temperature factor coefficients of the non*-H *atoms for* $Sn(CH_3)_4$

The temperature factors are expressed in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$.

| | Wyckoff notation | $x$ | $y$ | $z$ |
|---|---|---|---|---|
| Sn | 8(*c*) | 0·13023 (3) | 0·13023 | 0·13023 |
| C(1) | 8(*c*) | 0·2386 (4) | 0·2386 | 0·2386 |
| C(2) | 24(*d*) | 0·0200 (5) | 0·0205 (4) | 0·2408 (5) |
| H(1) | 24(*d*) | 0·189 | 0·288 | 0·288 |
| H(2) | 24(*d*) | −0·030 | 0·070 | 0·290 |
| H(3) | 24(*d*) | −0·030 | −0·030 | 0·192 |
| H(4) | 24(*d*) | 0·070 | −0·030 | 0·290 |

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Sn | 0·0264 (4) | 0·0264 | 0·0264 | −0·0002 (1) | −0·0002 | −0·0002 |
| C(1) | 0·034 (2) | 0·034 | 0·034 | −0·003 (2) | −0·003 | −0·003 |
| C(2) | 0·046 (3) | 0·036 (3) | 0·037 (3) | 0·005 (2) | 0·004 (2) | −0·007 (3) |

Table 2. *Interatomic distances* (Å) *and angles* (°) *for* $Sn(CH_3)_4$

| | | Corrected |
|---|---|---|
| Sn–C(1) | 2·102 (8) | 2·108 |
| Sn–C(2) | 2·138 (6) | 2·146 |
| C(1)–Sn–C(2) | 109·3 (2) | |
| C(2)–Sn–C(2$^{i}$) | 109·6 (2) | |

Symmetry code: (i) $z, x, y$.

data of $Si(CH_3)_4$ (Brockway & Jenkins, 1936; Sheehan & Schomaker, 1952; Beagley, Monaghan & Hewitt, 1971), $Ge(CH_3)_4$ (Brockway & Jenkins, 1936; Hencher & Mustoe, 1975), $Sn(CH_3)_4$ (Brockway & Jenkins, 1936; Nagashima, Fujii & Kimura, 1973) and $Pb(CH_3)_4$ (Brockway & Jenkins, 1936; Wong & Schomaker, 1958; Oyamada, Iijima & Kimura, 1971) show the molecules to be undistorted tetrahedra in the gaseous state. In the course of investigations on low-temperature rotational tunnelling in the solid state of methyl groups in the series $M(CH_3)_4$ with $M =$ Si, Ge, Sn and Pb, more than one tunnel splitting and other anomalies in the nuclear magnetic resonance and inelastic neutron scattering experiments suggested non-equivalent methyl groups in $Sn(CH_3)_4$ (Müller-Warmuth, Duprée & Prager, 1984; Prager, Duprée & Müller-Warmuth, 1983). As these results, which are supported by vibrational spectra, might be caused by significant deviations from ideal tetrahedral symmetry in the solid state, a low-temperature single-crystal X-ray diffraction structure analysis of tetramethyltin was undertaken.

**Experimental.** Tetramethyltin (m.p. 218 K, b.p. 351 K) was purified by fractional distillation. Single crystals were obtained from the melt according to the following method: Within a closed glass vacuum line, *ca* 1 mg of the compound was distilled into the end of a 0·5 mm diameter Mark capillary drawn to a narrow tip. The sealed sample was mounted in the crystal position of the diffractometer and cooled to 158 K by the nitrogen stream of the standard cooling unit. Single crystals of good quality were obtained by micro-zone melting controlled through the standard adjusting microscope of the diffractometer. A narrow beam (∅ 0·3 mm) of warm air was directed at a right angle to the sample capillary and was moved slowly (1·0 mm min$^{-1}$) by a motor along the capillary starting at the fine end (Krebs & Mandt, 1975).

The sample crystal was cylindrical (∅ 0·42 mm), 0·90 mm in length. At 158 K the intensities of 1518 reflections, $+h$ (0–9), $+k$ (0–10), $+l$ (1–14) (one octant), were measured in the $2\theta$ range up to 54° on a Syntex $P2_1$ four-circle diffractometer (parallel graphite monochromator, Mo $K\alpha$ radiation, $\theta$–$2\theta$ scan, scan speed 3·0–29·3° min$^{-1}$ in $2\theta$, two check reflections every 99 reflections, 1·2% intensity variation). They were averaged to 514 unique reflections, 505 of which with $I > 1·96\sigma(I)$ were used for all calculations. The cell constant was refined from $2\theta$ values of 20 reflections in the range 28–38°. Empirical absorption corrections based on $\psi$-scans followed by a spherical

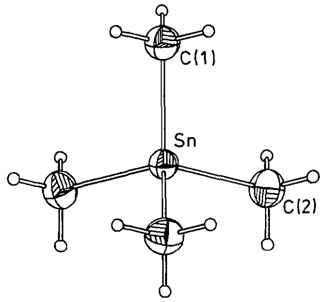

Fig. 1. $Sn(CH_3)_4$ molecule at 158 K with atomic numbering and vibrational ellipsoids (50% probability level). The threefold molecular axis is along Sn—C(1).

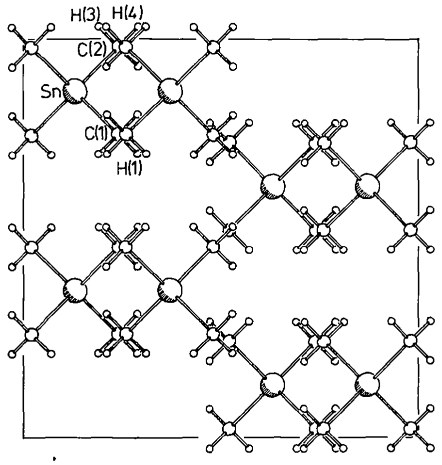

Fig. 2. Packing of the $Sn(CH_3)_4$ molecules in the unit cell.

correction were applied; true transmission factors were 0·28–0·58. The space group $Pa3$ was derived from the Laue symmetry $m3$ and the systematic absences for $0kl$ with $k = 2n + 1$.

From the Patterson synthesis it became apparent that the structure belongs to the $SnI_4$ structure type (Dickinson, 1923; Meller & Fankuchen, 1955). Starting with the coordinates of $SnI_4$ the structure was refined on $F$ (full matrix) with anisotropic temperature factors for Sn and C; coordinates for the H atoms were taken from a difference Fourier synthesis, the isotropic temperature factors of the H atoms being tied to the $U_{eq}$ values of the bonded C atoms with $U(\mathrm{H}) = 1{\cdot}2\, U_{eq}(\mathrm{C})$. The refinement of the H-atom coordinates did not show any significant deviations from an ideal staggered conformation and from ideal tetrahedral bond angles at the C atoms within the rather large limits of error. Accordingly, in the final stages of refinement, rigid methyl groups with $d(\mathrm{C—H}) = 0{\cdot}96$ Å and with ideal tetrahedral angles were used. The weighting scheme was $w^{-1} = [\sigma(F_o)]^2 + (0{\cdot}008\,|F_o|)^2$. Scattering factors for neutral atoms (H: bonded atoms) were taken from *International Tables for X-ray Crystallography* (1974). The final residuals were $R = 0{\cdot}050$, $wR = 0{\cdot}058$. All calculations were performed using the *EXTL* (Syntex, 1976) program system and the *SHELXTL* system (Sheldrick, 1981). $(\Delta/\sigma)_{\max} = 0{\cdot}01$, max. and min. heights in the final difference map 1·1 and −0·5 e Å$^{-3}$.

**Discussion.** The atomic parameters with their e.s.d.'s and temperature factor coefficients are given in Table 1.* Bond lengths and bond angles are shown in Table 2. The Sn—C bond lengths have been corrected according to a librational analysis, using the method of Schomaker & Trueblood (1968). In Fig. 1 the molecule is drawn with vibrational ellipsoids, Fig. 2 shows the orientation of the molecules in the unit cell.

According to the space group, the molecule has a threefold axis as the symmetry element. The most relevant feature of the molecular structure is the small but significant difference in the Sn—C(1) and Sn—C(2) distances (Table 2), indicating the distortion of the tetrahedral molecular framework. It is suggested that this distortion is due to packing forces rather than to intrinsic electronic properties of the $SnC_4$ bonding system. The almost ideal tetrahedral C—Sn—C angles show that there is no additional angular distortion of the framework. The average Sn—C bond length of 2·129 Å (corrected: 2·137 Å) is in good accordance with the 295 K value of 2·143 (5) Å in the structure of tetraphenyltin (Engelhardt, Leung, Raston & White, 1982; Chieh & Trotter, 1970; Akhmed & Aleksandrov, 1970) and with the electron diffraction $r_g$ value of 2·143 (3) Å in the $Sn(CH_3)_4$ molecule in the gas phase. The limited precision of the H-atom parameters does not allow a detailed vibrational analysis of the methyl groups. However, there is no question that, at the temperature of this investigation, there is no free rotation of the methyl groups, and that the librational motions of the methyl groups around the Sn—C bonds are quite limited. The shortest intermolecular contacts in the crystal structure are observed at H···H distances of 2·59, 2·60 and 2·65 Å, these values being close to the sum of the van der Waals radii. From DSC measurements and Guinier–Simon powder diffraction data between room temperature and 130 K, there is no indication of any phase transition in solid tetramethyltin.

The results of the structure determination support the conclusions on the dynamic behaviour of solid $Sn(CH_3)_4$, drawn from inelastic neutron scattering and NMR investigations (Prager, Duprée & Müller-Warmuth, 1983).

Stimulating discussions with Professor W. Müller-Warmuth are gratefully acknowledged. We also thank the Fonds der Chemischen Industrie for support of this work.

### References

Akhmed, N. A. & Aleksandrov, G. G. (1970). *Zh. Strukt. Khim.* **11**, 891–894.

Beagley, B., Monaghan, J. J. & Hewitt, T. G. (1971). *J. Mol. Struct.* **8**, 401–411.

Brockway, L. O. & Jenkins, H. O. (1936). *J. Am. Chem. Soc.* **58**, 2036–2044.

Chieh, P. C. & Trotter, J. (1970). *J. Chem. Soc. A*, pp. 911–914.

Dickinson, R. G. (1923). *J. Am. Chem. Soc.* **45**, 958–962.

Engelhardt, L. M., Leung, W.-P., Raston, C. L. & White, A. H. (1982). *Aust. J. Chem.* **35**, 2383–2384.

Hencher, J. L. & Mustoe, F. J. (1975). *Can. J. Chem.* **53**, 3542–3544.

*International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 99 ff. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Krebs, B. & Mandt, J. (1975). *Chem. Ber.* **108**, 1130–1137.

Meller, F. & Fankuchen, I. (1955). *Acta Cryst.* **8**, 343–344.

Müller-Warmuth, W., Duprée, K.-H. & Prager, M. (1984). *Z. Naturforsch. Teil A*, **39**, 66–79.

Nagashima, M., Fujii, H. & Kimura, M. (1973). *Bull. Chem. Soc. Jpn*, **46**, 3708–3711.

Oyamada, T., Iijima, T. & Kimura, M. (1971). *Bull. Chem. Soc. Jpn*, **44**, 2638–2642.

Prager, M., Duprée, K.-H. & Müller-Warmuth, W. (1983). *Z. Phys. B*, **51**, 309–318.

Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* B**24**, 63–76.

Sheehan, W. F. & Schomaker, V. (1952). *J. Am. Chem. Soc.* **74**, 3956.

Sheldrick, G. M. (1981). *Nicolet SHELXTL Operations Manual*, revision 3. Nicolet XRD Corporation, Cupertino, California, USA.

Syntex (1976). *EXTL Structure Determination System*. Syntex Analytical Instruments, Cupertino, California, USA.

Wong, C. & Schomaker, V. (1958). *J. Chem. Phys.* **28**, 1007–1009.

---

* The list of structure factors has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51718 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.