carboxylate groups make up the corners of the tetrahedron around the Sn and there is a weak carbonyl O···Sn contact [2·768 (4) Å]. The C—Sn—C angles are opened up [110·5 (2), 113·8 (2), 118·5 (3)°] whereas the O—Sn—C angles are compressed [93·9 (3), 107·9 (2), 109·3 (2)°]. The thienyl ring is flat [sum of internal angles is 540 (3)°] and is coplanar with the C(=O)—O [dihedral angle = 4 (3)°] fragment. The aromatic ring and carboxylate group in the corresponding triphenyltin benzoate esters are also coplanar with the exception of polymeric triphenyltin 2-chlorobenzoate, whose two planes are twisted by about 60° (Holmes, Day, Chandrasekhar, Vollano & Holmes, 1986*b*).

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### References

DAVIES, A. G. & SMITH, P. J. (1982). In *Comprehensive Organometallic Chemistry*, edited by G. WILKINSON, F. G. A. STONE & E. W. ABEL. New York: Pergamon Press.

FRENZ, B. A. (1985). *Structure Determination Package*. B. A. Frenz & Associates, Inc., College Station, Texas 77840, USA, and Enraf–Nonius, Delft, The Netherlands.

HARRISON, P. G., LAMBERT, K., KING, T. J. & MAJEE, B. (1983). *J. Chem. Soc. Dalton Trans.* pp. 363–369.

HOLMES, R. R., DAY, R. O., CHANDRASEKHAR, V., VOLLANO, J. F. & HOLMES, J. M. (1986*a*). Unpublished work cited in SMITH, P. J., DAY, R. O., CHANDRASEKHAR, V., HOLMES, J. M. & HOLMES, R. R. (1986). *Inorg. Chem.* **25**, 2495–2499.

HOLMES, R. R., DAY, R. O., CHANDRASEKHAR, V., VOLLANO, J. F. & HOLMES, J. M. (1986*b*). *Inorg. Chem.* **25**, 2490–2494.

NG, S. W., CHEN WEI & KUMAR DAS, V. G. (1988). *J. Organomet. Chem.* **345**, 59–64.

SANDHU, G. K. & VERMA, S. P. (1986). *Polyhedron*, **6**, 587–592.

SWISHER, R. G., VOLLANO, J. F., CHANDRASEKHAR, V., DAY, R. O. & HOLMES, R. R. (1984). *Inorg. Chem.* **23**, 3147–3152.

VOLLANO, J. F., DAY, R. O., RAU, D. N., CHANDRASEKHAR, V. & HOLMES, R. R. (1984). *Inorg. Chem.* **23**, 3153–3160.

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# Structure of Triphenyltin(IV) 3-Pyridinecarboxylate

BY SEIK WENG NG AND V. G. KUMAR DAS

*Institute of Advanced Studies and Department of Chemistry, University of Malaya,* 59100 *Kuala Lumpur, Malaysia*

AND F. VAN MEURS, J. D. SCHAGEN AND L. H. STRAVER

*PHI Application Laboratory, Scientific Instrument Division, B.V. Enraf–Nonius Delft, PO Box* 483, 2600 *Delft, The Netherlands*

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**Abstract.** [$(C_6H_5)_3SnOC(O)C_5H_4N$], $M_r = 472·11$, tetragonal, $P4_1$, $a = 12·075\ (2)$, $c = 14·629\ (2)$ Å, $V = 2133\ (1)$ Å$^3$, $Z = 4$, $D_x = 1·469$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71073 Å, $\mu = 12·2$ cm$^{-1}$, $F(000) = 944$, $T = 296\ (1)$ K, final $R = 0·028$ for 1427 reflections. The geometry at Sn is *trans*-$C_3SnNO$ trigonal bipyramidal and the Sn is displaced out of the equatorial plane by 0·118 (1) Å in the direction of the O. The molecules are linked by intermolecular Sn←:N [2·568 (7) Å] bridges. The pyridine ring of one molecule and the pyridine ring of the adjacent molecule are coplanar [dihedral angle 179 (6)°].

**Introduction.** Triorganotin esters of carboxylic acids are often five-coordinate polymers because of carboxylate bridging but the benzoate-type triphenyltin esters are generally monomeric (Ng, Kumar Das, van Meurs, Schagen & Straver, 1989). Stannyl esters of 2-pyrrole- (Sandhu & Verma, 1986) and 2-pyridine- (Harrison & Phillips, 1975) carboxylic acids appear to be carboxylate-bridged on spectroscopic evidence (IR, tin-119*m* Mössbauer) but nitrogen-bridged structures have been inferred for tri-*n*-butyltin 3- and 4-pyridinecarboxylates (Allen, Brooks, Formstone, Crowe & Smith, 1978). In the crystal structure of trimethyltin 2-pyridinecarboxylate monohydrate, the water is coordinated to tin and the molecules are hydrogen bonded into a three-dimensional lattice (Harrison & Phillips, 1979). A stretched helical nitrogen-bridged polymeric configuration is predicted for the title compound, triphenyltin 3-pyridinecarboxylate (nicotinate), from its variable-temperature Mössbauer spectrum ($80 \leq T \leq 130$ K; $a$ $-2·02 \times 10^{-1}$ K$^{-1}$) (Ng & Kumar Das, 1988). The present crystal-structure study was aimed at corroborating the spectral finding.

**Experimental.** The title compound was prepared by mixing stoichiometric quantities of nicotinic acid and

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triphenyltin hydroxide in ethanol; m.p. 463 K. A crystal measuring 0·30 × 0·15 × 0·12 mm was mounted on an Enraf–Nonius CAD-4 diffractometer for the data collection. The maximum $2\theta$ angle was 48°; $-13 < h < 13$, $0 < k < 13$, $0 < l < 166$. Details of the experimental and computational methods have been described (Ng, Kumar Das, van Meurs, Schagen & Straver, 1989). Of the 1756 unique reflections collected, 1427 were included in the least-squares refinement cycles that converged at an $R$ factor of 0·028 ($wR$ = 0·30); the 'fudge factor' was 0·05; goodness of fit = 1·15. H atoms were not located. The convergence:largest shift

Table 1. *Atomic coordinates for triphenyltin 3-pyridinecarboxylate*

| | $x$ | $y$ | $z$ | $B_{eq}$(Å$^2$) |
|---|---|---|---|---|
| Sn | 0·54423 (4) | −0·00726 (5) | 0·06200 (5) | 5·55 (1) |
| O(1) | 0·4495 (5) | 0·0386 (6) | 0·1794 (4) | 6·8 (2) |
| O(2) | 0·2879 (5) | 0·0565 (5) | 0·1115 (5) | 6·9 (2) |
| N | 0·3213 (5) | 0·0604 (6) | 0·4333 (5) | 6·1 (2) |
| C(1) | 0·3456 (6) | 0·0554 (6) | 0·1787 (6) | 4·8 (2) |
| C(11) | 0·6830 (6) | −0·0051 (7) | 0·1519 (6) | 5·3 (2) |
| C(12) | 0·7449 (9) | −0·1016 (9) | 0·1712 (9) | 9·9 (3) |
| C(13) | 0·8331 (10) | −0·0935 (12) | 0·2342 (10) | 12·0 (4) |
| C(14) | 0·8607 (9) | 0·0047 (11) | 0·2765 (9) | 10·6 (4) |
| C(15) | 0·8081 (10) | 0·0957 (10) | 0·2521 (8) | 11·1 (3) |
| C(16) | 0·7151 (10) | 0·0946 (10) | 0·1891 (8) | 9·7 (3) |
| C(21) | 0·4621 (6) | −0·1628 (7) | 0·0406 (7) | 6·4 (2) |
| C(22) | 0·4421 (8) | −0·2287 (8) | 0·1164 (8) | 8·0 (3) |
| C(23) | 0·3884 (9) | −0·3317 (9) | 0·1089 (11) | 10·5 (4) |
| C(24) | 0·3584 (8) | −0·3673 (9) | 0·0230 (11) | 10·8 (4) |
| C(25) | 0·3761 (9) | −0·3047 (10) | −0·0536 (10) | 10·3 (4) |
| C(26) | 0·4273 (8) | −0·1962 (9) | −0·0465 (9) | 8·7 (3) |
| C(31) | 0·5144 (8) | 0·1381 (8) | −0·0181 (7) | 6·6 (2) |
| C(32) | 0·5983 (10) | 0·2086 (9) | −0·0349 (9) | 9·5 (3) |
| C(33) | 0·5812 (12) | 0·3081 (10) | −0·0897 (9) | 11·5 (4) |
| C(34) | 0·4764 (12) | 0·3256 (10) | −0·1262 (10) | 11·3 (4) |
| C(35) | 0·3997 (11) | 0·2480 (13) | −0·1140 (11) | 15·0 (4) |
| C(36) | 0·4135 (10) | 0·1511 (12) | −0·0614 (9) | 12·6 (4) |
| C(41) | 0·2962 (6) | 0·0715 (6) | 0·2719 (6) | 5·4 (2) |
| C(42) | 0·2189 (8) | 0·1004 (8) | 0·4449 (8) | 7·6 (3) |
| C(43) | 0·1515 (8) | 0·1285 (8) | 0·3709 (9) | 8·1 (3) |
| C(44) | 0·1895 (7) | 0·1134 (7) | 0·2802 (7) | 6·5 (2) |
| C(45) | 0·3586 (6) | 0·0471 (6) | 0·3485 (6) | 5·5 (2) |

$B_{eq} = (4/3)[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}]$.

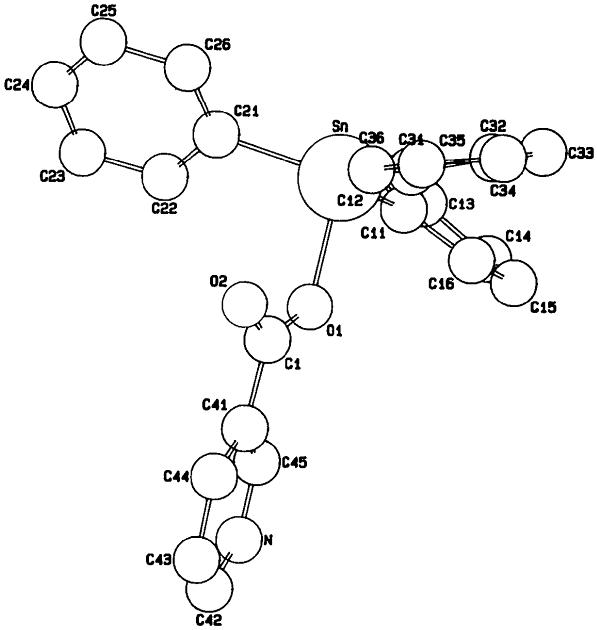

Fig. 1. Asymmetric unit of triphenyltin 3-pyridinecarboxylate.

Table 2. *Bond distances* (Å) *and bond angles* (°) *for triphenyltin 3-pyridinecarboxylate*

| | | | | | |
|---|---|---|---|---|---|
| Sn—O(1) | 2·137 (6) | Sn—N$^{i}$ | 2·568 (7) | Sn—C(11) | 2·130 (8) |
| Sn—C(21) | 2·147 (8) | Sn—C(31) | 2·140 (10) | Sn···O(2) | 3·271 (6) |
| C(11)—C(12) | 1·41 (1) | C(12)—C(13) | 1·41 (2) | C(13)—C(14) | 1·38 (2) |
| C(14)—C(15) | 1·32 (2) | C(15)—C(16) | 1·45 (2) | C(16)—C(11) | 1·38 (1) |
| C(21)—C(22) | 1·39 (1) | C(22)—C(23) | 1·41 (1) | C(23)—C(24) | 1·38 (2) |
| C(24)—C(25) | 1·37 (2) | C(25)—C(26) | 1·45 (2) | C(26)—C(21) | 1·40 (2) |
| C(31)—C(32) | 1·35 (1) | C(32)—C(33) | 1·46 (2) | C(33)—C(34) | 1·39 (2) |
| C(34)—C(35) | 1·33 (2) | C(35)—C(36) | 1·41 (2) | C(36)—C(31) | 1·38 (2) |
| O(1)—C(1) | 1·270 (9) | C(1)—O(2) | 1·21 (1) | C(1)—C(41) | 1·50 (1) |
| C(41)—C(45) | 1·38 (1) | C(45)—N | 1·33 (1) | N—C(42) | 1·34 (1) |
| C(42)—C(43) | 1·40 (2) | C(43)—C(44) | 1·42 (2) | C(44)—C(41) | 1·39 (1) |
| | | | | | |
| O(1)—Sn—N$^{i}$ | 173·1 (2) | O(1)—Sn—C(11) | 85·5 (3) | O(1)—Sn—C(21) | 95·5 (3) |
| O(1)—Sn—C(13) | 97·9 (3) | N$^{i}$—Sn—C(11) | 87·6 (3) | N$^{i}$—Sn—C(21) | 88·1 (3) |
| N$^{i}$—Sn—C(31) | 84·9 (3) | C(11)—Sn—C(21) | 117·7 (3) | C(11)—Sn—C(31) | 117·4 (4) |
| C(21)—Sn—C(31) | 124·0 (5) | Sn—C(11)—C(12) | 122·0 (8) | Sn—C(11)—C(16) | 118·4 (8) |
| C(11)—C(12)—C(13) | 118 (1) | C(12)—C(13)—C(14) | 122 (2) | C(13)—C(14)—C(15) | 119 (1) |
| C(14)—C(15)—C(16) | 122 (1) | C(15)—C(16)—C(11) | 118 (1) | C(16)—C(11)—C(12) | 120 (1) |
| Sn—C(21)—C(22) | 117·8 (8) | Sn—C(21)—C(26) | 121·5 (9) | C(21)—C(22)—C(23) | 122 (1) |
| C(22)—C(23)—C(24) | 118 (1) | C(23)—C(24)—C(25) | 122 (1) | C(24)—C(25)—C(26) | 120 (2) |
| C(25)—C(26)—C(21) | 117 (1) | C(26)—C(21)—C(22) | 121 (1) | Sn—C(31)—C(32) | 119·5 (9) |
| Sn—C(31)—C(36) | 119·5 (9) | C(31)—C(32)—C(33) | 121 (1) | C(32)—C(33)—C(34) | 118 (1) |
| C(33)—C(34)—C(35) | 118 (1) | C(34)—C(35)—C(36) | 125 (1) | C(35)—C(36)—C(31) | 117 (1) |
| C(36)—C(31)—C(32) | 120 (1) | Sn—N$^{i}$—C(42$^{i}$) | 125·6 (7) | Sn—N$^{i}$—C(45$^{i}$) | 116·0 (5) |
| N—C(42)—C(43) | 122 (1) | C(42)—C(43)—C(44) | 120·4 (9) | C(43)—C(44)—C(41) | 115·4 (9) |
| C(44)—C(41)—C(45) | 120·8 (8) | C(41)—C(45—N | 123·1 (7) | C(45)—N—C(42) | 118·4 (8) |
| Sn—O(1)—C(1) | 124·3 (6) | O(1)—C(1)—O(2) | 125 (1) | O(1)—C(1)—C(41) | 113·9 (3) |
| O(2)—C(1)—C(41) | 120·6 (9) | C(1)—C(41)—C(44) | 119·7 (8) | C(1)—C(41)—C(45) | 119·5 (8) |

Symmetry code: (i) $1-x, -y, z-0{\cdot}5$.

ratio was less than 0·01. In the final difference map, the highest peak was 0·27 (4) and the lowest peak was −0·24 (4) e Å$^{-3}$. The atomic coordinates are listed in Table 1 and bond distances and angles in Table 2.*

**Discussion.** The geometry and atom labeling for the asymmetric unit of triphenyltin 3-pyridinecarboxylate are shown in Fig. 1. The coordination polyhedron around the Sn atom is trigonal bipyramidal, with the *ipso*-carbons of the phenyl groups forming the trigonal plane. The apical positions are occupied by the O of the carboxylate group and the N of the neighbouring pyridyl ring (symmetry transformation: $1-x$, $-y$, $z-0{\cdot}5$). The Sn atom is displaced by 0·118 (1) Å out of the trigonal plane towards the O atom. The Sn—N′ bond is 2·568 (7) Å and the intramolecular Sn···O(2) contact is 3·271 (6) Å. The plane of the carboxylate group is twisted by 13·7 (5)° with respect to that of the pyridyl ring. The $Sn—O—C(=O)—C_5H_4N$ fragment is virtually flat, so that the polymer appears to be propagating on the plane that is passing through the pyridyl rings.

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### References

ALLEN, D. W., BROOKS, J. S., FORMSTONE, R., CROWE, A. J. & SMITH, P. J. (1978). *J. Organomet. Chem.* **156**, 359–368.
HARRISON, P. G. & PHILLIPS, R. C. (1975). *J. Organomet. Chem.* **99**, 79–92.
HARRISON, P. G. & PHILLIPS, R. C. (1979). *J. Organomet. Chem.* **182**, 37–46.
NG, S. W. & KUMAR DAS, V. G. (1988). Unpublished results.
NG, S. W., KUMAR DAS, V. G., VAN MEURS, F., SCHAGEN, J. D. & STRAVER, L. H. (1989). *Acta Cryst.* C**45**, 568–570.
SANDHU, G. K. & VERMA, S. P. (1986). *Polyhedron*, **6**, 587–592.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51525 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# Structure of the Organic Superconductor $(DMET)_2AuI_2$

BY YOSHIMITSU ISHIKAWA, KOICHI KIKUCHI, KAZUYA SAITO AND ISAO IKEMOTO

*Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Fukazawa, Setagaya-ku, Tokyo 158, Japan*

AND KEIJI KOBAYASHI

*Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153, Japan*

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**Abstract.** 2-(4,5-Dimethyldiselenol-2-ylidene)-5,6-dihydrodithiolo[4,5-*b*]dithiin diiodoaurate(I) (2:1), $(C_{10}H_{10}S_4Se_2)_2.[AuI_2]$, $M_r = 1283{\cdot}48$, triclinic, $P\bar{1}$, $a = 6{\cdot}722$ (1), $b = 7{\cdot}724$ (3), $c = 15{\cdot}776$ (2) Å, $\alpha = 90{\cdot}02$ (2), $\beta = 98{\cdot}35$ (1), $\gamma = 75{\cdot}71$ (2)°, $V = 784{\cdot}7$ (4) Å$^3$, $Z = 1$, $D_x = 2{\cdot}72$ Mg m$^{-3}$, $\mu$(Mo $K\alpha$) = 11·75 mm$^{-1}$, $F(000) = 589$, $T = 297$ K, $R = 0{\cdot}049$ for 2574 reflections. The structure consists of sheets of DMET ($C_{10}H_{10}S_4Se_2$) and of $AuI_2$. The DMET molecules form ordered stacks within the sheet. There are some short intermolecular contacts not only within the stacks but also between the stacks. The structure is very similar to that of $(DMET)_2I_3$, but is different from that of $(DMET)_2Au(CN)_2$ in the relative position of anions with respect to DMET molecules.

**Introduction.** We have recently discovered some superconductors based on an unsymmetrical donor DMET (Kikuchi, Kikuchi, Namiki, Saito, Ikemoto, Murata, Ishiguro & Kobayashi, 1987; Kikuchi, Murata, Honda, Namiki, Saito, Kobayashi, Ishiguro & Ikemoto, 1987; Kikuchi, Murata, Honda, Namiki, Saito, Ishiguro, Kobayashi & Ikemoto, 1987; Kikuchi, Murata, Honda, Namiki, Saito, Anzai, Kobayashi, Ishiguro & Ikemoto, 1987; Kikuchi, Honda, Ishikawa, Saito, Ikemoto, Murata, Anzai, Ishiguro & Kobayashi, 1988). Besides superconductivity, DMET salts exhibit a variety of properties depending on the anions and can be classified into five groups on the basis of temperature-dependence of resistivity (Murata, Kikuchi, Takahashi, Kobayashi, Honda, Saito, Kanoda, Tokiwa, Anzai, Ishiguro &

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