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# Skew-trapezoidal bipyramidal diorganotin(IV) bischelates. Crystal structure of dimethylbis(2-pyridinethiolato-*N*-oxide)tin(IV)

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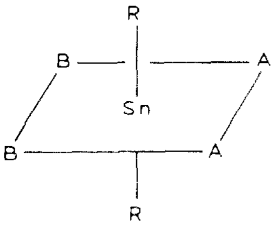
## Abstract

Dimethylbis(2-pyridinethiolato-*N*-oxide)tin(IV), $Me_2Sn(2\text{-}SPyO)_2$, crystallizes in space group $P2_1/c$ with $a$ 9.877(3), $b$ 11.980(4), $c$ 13.577(3) Å, $\beta$ 109.1(2)° and $Z = 4$. The structure was refined to $R_F = 0.036$ for 2263 Mo-$K_\alpha$ observed reflections. The coordination geometry at tin is a skew-trapezoidal bipyramid, with the oxygen [Sn–O 2.356(3), 2.410(4) Å] and sulfur [Sn–S 2.536(1), 2.566(1) Å] atoms of the chelating groups occupying the trapezoidal plane and the methyl groups [Sn–C 2.106(6), 2.128(7) Å] occupying the apical positions. The methyl–tin–methyl skeleton is bent [C–Sn–C 138.9(2)°]. The S–Sn–S angle is 77.8(1)°, but the O–Sn–O angle is opened to 136.7(1)° to accommodate the intruding methyl groups. The carbon–tin–carbon angles predicted from quadrupole splitting ($^{119m}$Sn Mössbauer) and one-bond $^{119}$Sn–$^{13}$C coupling constant (solution $^{13}$C NMR) data agree closely with the experimental value.

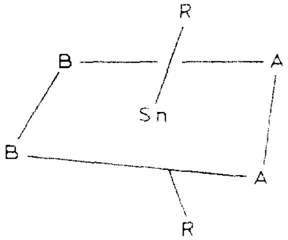
## Introduction

Although there are many examples of six-coordinated diorganotin(IV) bischelates in the literature, the factors governing the geometry at the tin center are not well-understood. The $C_2Sn$ skeletal configurations in these structures have been described, often vaguely, as being distorted *cis* or *trans*, with little identification of the influence exerted by the chelate moieties on the stereochemical disposition of the Sn–C bonds. For the six-coordinate $R_2Sn(A\text{–}B)_2$ compound, where A–B represents a uninegative bidentate chelate with the negative charge residing on B, a distorted octahedral geometry with carbon–tin–carbon bond angles lying in the range 135–155° has been given the label 'skew-trapezoidal bipyramid' [1]. Carbon–tin–carbon angles have been correlated with the $^{119m}$Sn Mössbauer



Octahedral

$O_h$



Skew-trapezoidal bipyramidal

STB

quadrupole splitting values [2] and very recently, with one-bond $^{119}$Sn–$^{13}$C NMR coupling constants [3]; these spectral parameters appear to respond in an orderly way to hybridization and related changes at the tin atom.

The skew-trapezoidal bipyramid can be envisaged as a distortion of a regular *trans* octahedron, characterized by an opening of the A–Sn–A angle and inclination of the Sn–R bonds towards the A–A edge. Additional widening of the A–Sn–A angle and elongation of the Sn–A bonds lead eventually to a tetrahedral geometry. This distortion from the $O_h$ towards the STB geometry is especially favored if the chelate bite angle (A–Sn–B) is small [4,5]. For $\mathrm{Me_2Sn(acac)_2}$ (acac = actylacetonate) [6], n-$\mathrm{Bu_2Sn(dbzm)_2}$ (dbzm = anion of dibenzoylmethane) [7] and $\mathrm{Ph_2Sn[S_2P(O\text{-}i\text{-}Pr)_2]_2}$ [8] where the bite angles are large (76–86°), undistorted *trans*-[$\mathrm{R_2Sn}$] angles of 180° have been found. The bischelates $\mathrm{Me_2Sn(trop)_2}$ (trop = tropolonate) [9], $\mathrm{Me_2Sn[MeC(O)N(H)O]_2}$ [10], $\mathrm{Me_2Sn(Oxin)_2}$ (Oxin = 8-hydroxyquinolinate) [11], $\mathrm{Me[(Me_3Si)_2CH]Sn(Oxin)_2}$ [12], ($p$-$\mathrm{ClC_6H_4}$)($p$-$\mathrm{MeC_6H_4}$)$\mathrm{Sn(Oxin)_2}$ [13] and $\mathrm{Ph_2Sn(S_2CNEt_2)_2}$ [14] are distorted towards the *cis* configuration, with C–Sn–C angles between 101 and 109°. Intermediate '*trans*' values for the $\mathrm{R_2Sn}$ angle in the range 122–157° have been reported for $\mathrm{Me_2Sn[MeC(O)N(H)O]_2 \cdot H_2O}$ [10], $\mathrm{Me_2Sn[MeC(O)N(Me)O]_2}$ [15], $\mathrm{Me_2Sn(NO_3)_2}$ [16], Et(n-Pr)$\mathrm{Sn(MeOxin)_2}$ (MeOxin = 2-methyl-8-hydroxyquinolinate) [17], $\mathrm{Me_2Sn(S_2COEt)_2}$ [18], $\mathrm{Me_2Sn(S_2CNMe_2)_2}$ [19], $\mathrm{Me_2Sn(S_2CNEt_2)_2}$ (three crystal modifications) [20,21], $\mathrm{Me_2Sn[S_2CN(CH_2)_4]_2}$ [22], n-$\mathrm{Bu_2Sn[S_2CN(C_4H_8)O]_2}$ [23], $\mathrm{Me_2Sn(S_2PMe_2)_2}$ [24], $\mathrm{Me_2Sn(S_2PO_2C_2Me_4)_2}$ [25], $\mathrm{Ph_2Sn[S_2P(OEt)_2]_2}$ [26], $\mathrm{Me_2Sn(S_2AsMe_2)_2}$ [27] and n-$\mathrm{Bu_2Sn(5\text{-}NO_2\text{-}2\text{-}SPy)_2}$ (2-SPy = 2-pyridinethiolate) [28]. The Sn–S (3.515 Å) and Sn–N (2.77 Å) bonds in the last two examples are long enough for the molecules to be essentially four-coordinate *.

When a chelate binds to a triorganotin, as in $\mathrm{Ph_3Sn(dbzm)}$ [29], $\mathrm{Me_3Sn[PhC(O)N(Ph)O]}$ [30], $\mathrm{Ph_3Sn[PhC(O)N(Ph)O]}$ [31] and $\mathrm{Ph_3Sn}$(8-quinolinethiolate) [32], *cis*-trigonal bipyramidal geometries are observed. However, a unique square pyramidal geometry at tin has been found in tribenzyl(2-pyridinethiolato-*N*-oxide)tin (see preceding paper). The structure of $\mathrm{Me_2Sn(2\text{-}SPyO)_2}$ (2-SPyO = anion of 2-pyridinethiol *N*-oxide) was determined to find out if the geometry at tin in this species might also be unusual.

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* *Note added in proof*: A long Sn···S bond of 3.607 Å has recently been reported (O.-S. Jung, Y.S. Sohn and J.A. Ibers, Inorg. Chem., 25 (1986) 2273) in trigonal bipyramidal $\mathrm{[t\text{-}Bu_2SnSC(S)NHCH_2CH_2NHC(S)S]_2 \cdot 4THF}$.

Table 1

Data collection and processing parameters for dimethylbis(2-pyridinethiolato-*N*-oxide)tin(IV)

| | |
|---|---|
| Molecular formula | $C_{12}H_{14}N_2O_2S_2Sn$ |
| Molecular weight | 401.07 |
| Cell constants | $a$ 9.877(3) Å  $\beta$ 109.01(2)° |
| | $b$ 11.980(4) Å  $V$ 1518.9(7) $Å^3$ |
| | $c$ 13.577(3) Å  $Z = 4$ |
| Density (exptl) | 1.75 g $cm^{-3}$ (flotation in $ZnBr_2/H_2O$) |
| Density (calcd) | 1.754 g $cm^{-3}$ |
| Space group | $P2_1/c$ |
| Radiation | graphite-monochromatized Mo-$K_\alpha$ ($\lambda$ 0.71069 Å) |
| Absorption coefficient | 19.50 $cm^{-1}$ |
| Crystal size | $0.30 \times 0.26 \times 0.12$ $mm^3$ |
| Mean $\mu r$ | 0.20 |
| Transmission factors | 0.598–0.671 |
| Scan speed and type | $\omega$–$2\theta$; 2.02–8.37 deg $min^{-1}$ |
| Scan range | 1° below $K_{\alpha_1}$ to 1° above $K_{\alpha_2}$ |
| Background counting | stationary counts for 1/2 scan time at each end of scan |
| Collection range | $h$, $k$, $\pm l$; $2\theta_{max} = 52°$ |
| Unique data measured | 2673 |
| Observed data with $\vert F_o \vert > 3\sigma(\vert F_o \vert)$, $n$ | 2263 |
| Number of variables, $p$ | 178 |
| $R_F = \Sigma \Vert F_o \vert - \vert F_c \Vert / \Sigma \vert F_o \vert$ | 0.036 |
| Weighting scheme | $w = [\sigma^2(F_o) + 0.0005 \vert F_o \vert^2]^{-1}$ |
| $R_G = [\Sigma w(\vert F_o \vert - \vert F_c \vert)^2 / \Sigma w \vert F_o \vert^2]^{1/2}$ | 0.043 |
| $S = [\Sigma w(\vert F_o \vert - \vert F_c \vert)^2 / (n - p)]^{1/2}$ | 1.296 |
| Residual extremes in final diff. map | +0.63 to −0.54 e $Å^{-3}$ |

Table 2

Atomic coordinates ($\times 10^5$ for Sn, $\times 10^4$ for other atoms) for dimethylbis(2-pyridinethiolato-*N*-oxide)tin(IV)

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Sn | 16619(3) | 17790(2) | 8431(3) |
| S(1) | 3740(2) | 3178(1) | 1386(1) |
| S(2) | 381(1) | 3600(1) | 898(1) |
| O(1) | 3855(4) | 766(3) | 1083(4) |
| O(2) | −797(4) | 1353(3) | 356(4) |
| N(1) | 5113(4) | 1223(3) | 1547(3) |
| N(2) | −1781(4) | 2153(3) | 90(3) |
| C(1) | 5242(5) | 2343(4) | 1720(3) |
| C(2) | 6594(5) | 2767(5) | 2156(4) |
| C(3) | 7776(5) | 2077(5) | 2422(4) |
| C(4) | 7617(5) | 953(5) | 2722(4) |
| C(5) | 6270(5) | 544(4) | 1830(4) |
| C(6) | −1395(5) | 3249(4) | 285(4) |
| C(7) | −2473(5) | 4043(4) | −6(4) |
| C(8) | −3871(5) | 3745(4) | −456(4) |
| C(9) | −4219(5) | 2630(4) | −621(4) |
| C(10) | −3157(5) | 1845(4) | −351(3) |
| C(11) | 1714(8) | 886(5) | 2210(5) |
| C(12) | 1390(7) | 1457(5) | −735(5) |

## Experimental

The title compound separated out when aqueous solutions of dimethyltin dichloride and sodium 2-pyridinethiolato-*N*-oxide were mixed in a 1/2 molar ratio. Recrystallization of the product from chloroform gave a tan-colored solid, m.p. 199–200 ° C. Anal. Found: C 35.94, H 3.50, N 6.58. $C_{12}H_{14}N_2O_2S_2Sn$ calc: C 35.94; H, 3.49; N, 6.99. An identical product was obtained when trimethyltin chloride was treated with a stoichiometric proportion of the sodium salt (Anal. Found: C, 35.84; H, 3.54; N, 6.90). Crystals suitable for X-ray diffraction were obtained upon slow crystallization from chloroform. $^1$H NMR ($CDCl_3$): $\delta(CH_3)$ 0.9 ppm, $^2J(^{119}Sn-C-^1H)$ 82.5 Hz; $^{13}C$ NMR ($CDCl_3$): $\delta(CH_3)$ 9.9 ppm, $^1J(^{119}Sn-^{13}C)$

Table 3

Bond lengths (Å), bond angles ( ° ), and selected torsion angles ( ° ) for dimethylbis(2-pyridinethiolato-*N*-oxide)tin(IV)

| | | | |
|---|---|---|---|
| Sn–S(1) | 2.566(1) | Sn–S(2) | 2.536(1) |
| Sn–O(1) | 2.410(4) | Sn–O(2) | 2.356(3) |
| Sn–C(11) | 2.128(7) | Sn–C(12) | 2.106(6) |
| S(1)–C(1) | 1.723(5) | S(2)–C(6) | 1.731(5) |
| O(1)–N(1) | 1.316(5) | O(2)–N(2) | 1.328(5) |
| N(1)–C(1) | 1.361(6) | N(2)–C(10) | 1.346(6) |
| N(2)–C(6) | 1.369(6) | N(2)–C(10) | 1.346(6) |
| C(1)–C(2) | 1.370(6) | C(2)–C(3) | 1.380(8) |
| C(3)–C(4) | 1.363(9) | C(4)–C(5) | 1.360(7) |
| C(6)–C(7) | 1.385(6) | C(7)–C(8) | 1.363(7) |
| C(8)–C(9) | 1.379(7) | C(9)–C(10) | 1.367(7) |
| S(1)–Sn–S(2) | 77.8(1) | S(1)–Sn–O(1) | 72.0(1) |
| S(2)–Sn–O(1) | 149.8(1) | S(1)–Sn–O(2) | 151.3(1) |
| S(2)–Sn–O(2) | 73.5(1) | O(1)–Sn–O(2) | 136.7(1) |
| S(1)–Sn–C(11) | 106.7(2) | S(2)–Sn–C(11) | 106.1(2) |
| O(1)–Sn–C(11) | 82.1(2) | O(2)–Sn–C(11) | 82.3(2) |
| S(1)–Sn–C(12) | 103.7(2) | S(2)–Sn–C(12) | 106.7(2) |
| O(1)–Sn–C(12) | 81.8(2) | O(2)–Sn–C(12) | 84.1(2) |
| C(11)–Sn–C(12) | 138.9(2) | Sn–S(1)–C(1) | 103.6(2) |
| Sn–S(2)–C(6) | 102.3(2) | Sn–O(1)–N(1) | 121.5(3) |
| Sn–O(2)–N(2) | 121.1(3) | O(1)–N(1)–C(1) | 120.9(4) |
| O(1)–N(1)–C(5) | 117.7(4) | C(1)–N(1)–C(5) | 121.4(4) |
| O(2)–N(2)–C(6) | 120.4(3) | O(2)–N(2)–C(10) | 117.8(4) |
| C(6)–N(2)–C(10) | 121.7(4) | S(1)–C(1)–N(1) | 120.2(3) |
| S(1)–C(1)–C(2) | 122.2(4) | N(1)–C(1)–C(2) | 117.6(4) |
| C(1)–C(2)–C(3) | 120.9(5) | C(2)–C(3)–C(4) | 120.4(5) |
| C(3)–C(4)–C(5) | 118.0(5) | N(1)–C(5)–C(4) | 121.6(5) |
| S(2)–C(6)–N((2) | 120.1(3) | S(2)–C(6)–C(7) | 122.3(3) |
| N(2)–C(6)–C(7) | 117.6(4) | C(6)–C(7)–C(8) | 121.4(4) |
| C(7)–C(8)–C(9) | 119.3(5) | C(8)–C(9)–C(10) | 119.6(4) |
| N(2)–C(10)–C(9) | 120.4(4) | | |
| Sn–O(1)–N(1)–C(1) | −13.3(7) | Sn–O(2)–N(2)–C(6) | −12.8(6) |
| O(1)–N(1)–C(1)–S(1) | 2.9(7) | O(2)–N(2)–C(6)–S(2) | −0.9(7) |
| N(1)–C(1)–S(1)–Sn | 7.1(4) | N(2)–C(6)–S(2)–Sn | 11.6(5) |
| C(1)–S(1)–Sn–O(1) | −8.6(2) | C(6)–S(2)–Sn–O(2) | −11.6(2) |
| S(1)–Sn–O(1)–N(1) | 12.8(4) | S(2)–Sn–O(2)–N(2) | 14.8(4) |

Table 4

Least-squares planes and dihedral angles

*Least-squares planes* [a]

| Plane No. | Atoms fitted | Equation of plane | | | | rms (Å×10$^3$) |
|---|---|---|---|---|---|---|
| | | $l$ | $m$ | $n$ | $d$ | |
| 1 | Sn, C(11), C(12) | 0.9874 | −0.1241 | −0.0985 | 1.208 | – |
| 2 | O(1), O(2), C(11), C(12) | 0.1756 | 0.9718 | 0.1572 | 1.629 | 69 |
| 3 | S(1), O(1), N(1), C(1)–C(5) | −0.0886 | −0.1337 | 0.9870 | −0.175 | 24 |
| 4 | S(2), O(2), N(2), C(6)–C(10) | −0.1139 | −0.0737 | 0.9908 | 0.703 | 16 |
| 5 | Sn, S(1), S(2), O(1), O(2) | 0.0950 | −0.1589 | 0.9827 | 0.410 | 13 |

*Dihedral angles between planes* [b]

| Planes | Angles (°) | Planes | Angles (°) |
|---|---|---|---|
| 1–2 | 87.9 | 1–3 | 99.7 |
| 1–4 | 101.6 | 1–5 | 89.0 |
| 2–3 | 89.4 | 2–4 | 86.3 |
| 2–5 | 89.0 | 3–4 | 3.7 |
| 3–5 | 10.6 | 4–5 | 13.0 |

[a] Plane equation is in the form $lX_0 + mY_0 + nZ_0 = d$, where $X_0$, $Y_0$, $Z_0$ are orthogonal coordinates in Å referred to axes $x_0$, $y_0$, $z_0$ respectively, with $x_0$ parallel to $a^*$, $y_0$ to $b$, and $z_0$ to $c$. [b] Standard deviation approx. 0.7°.

698.2 Hz; $\delta(C_5H_4NS)$ 118.8, 128.6, 129.1, 137.1, 157.2 ppm. Mössbauer data: Isomer shift 1.30, Quadrupole splitting 3.29, $\Gamma_1$ 1.00, $\Gamma_2$ 0.99 mm s$^{-1}$; $d[\ln A_T/\ln A_{80\,K}]/dT = -1.96 \times 10^{-2}$ K$^{-1}$ for $80 \leqslant T \leqslant 130$ (6 points, corr. coeff. = −0.996).

### *X-Ray crystallography*

Diffraction measurements were made on a Nicolet R3m four-circle diffractometer (graphite-monochromatized Mo-$K_\alpha$ radiation, λ 0.71069 Å). Details of the experimental and computational methods are as described in the preceding paper. Data collection and processing parameters are summarized in Table 1. Table 2 lists the atomic coordinates and Table 3 the bond lengths and angles and selected torsional angles. Least-squares planes and dihedral angles are given in Table 4. Lists of anisotropic thermal parameters and observed and calculated structure factors are available from the authors.

## Results and discussion

### *X-Ray*

*Trans*-dimethyl-*cis*-O,O′-*cis*-S,S′-bis(2-pyridinethiolato-*N*-oxide)tin(IV) is a discrete monomer as depicted in Fig. 1. The methyl groups subtend an angle of 138.9(2)° at tin, and the $C_2Sn$ plane is orthogonal to the plane containing the tin and the two sets of oxygen and sulfur atoms [dihedral angle 89.0(7)°]. The S(1)–Sn–S(2) angle is 77.8(1)°, but the O(1)–Sn–O(2) angle is opened to 136.7(1)°, as a consequence of the intruding methyl groups. The bite angles of the ligand are 72.0(1) and 73.5(1)°. As shown by the torsional angles (Table 3), the five-membered chelate rings are *gauche*, with appreciable folding of each planar 2-pyridinethiolate-*N*-oxide ligand about the corresponding non-bonded O · · · S line. If it were not for

*(Continued on p. 302)*

Table 5

Structural data for diorganotin bischelates [a]

| $R_2Sn(chelate)_2$ | R–Sn–R geometry | R–Sn–R angle (°) | A–Sn–A angle (°) | Chelate bite angle (°) | Sn–C (Å) | Sn–X (Å) | Ref. |
|---|---|---|---|---|---|---|---|
| $Me_2Sn(acac)_2$ | *trans* | 180 | 94 | 86 | 2.14 | 2.18, 2.20 | 6 |
| n-$Bu_2Sn(dbzm)_2$ | *trans* | 180 | 96.2 | 83.8 | 2.115 | 2.189, 2.199 | 7 |
| $Me_2Sn(trop)_2$ | *cis* | 108.2 | – | 72.3, 73.6 | 2.156, 2.173 | 2.143, 2.158, 2.180, 2.203 | 9 |
|  | *cis* | 109.0 | – | 72.6, 73.5 | 2.139, 2.175 | 2.134, 2.157, 2.177, 2.192 |  |
| $Me_2Sn[MeC(O)N(H)O]_2$ | *cis* | 109.1 | – | 81.5 | 2.144 | 2.106, 2.228 | 10 |
| $Me_2Sn[MeC(O)N(H)O]_2 \cdot H_2O$ | STB | 156.7 | 146.9 | 70.7, 72.1 | 2.16, 2.17 | 2.15, 2.15, 2.35, 2.49 | 10 |
|  | STB | 156.9 | 146.2 | 71.5, 71.7 | 2.14, 2.16 | 2.16, 2.17, 2.36, 2.43 |  |
| $Me_2Sn[MeC(O)N(Me)O]_2$ | STB | 145.84 | 144.07 | 71.11, 71.61 | 2.105, 2.113 | 2.107, 2.126, 2.374, 2.384 | 15 |
| $Me_2Sn(NO_3)_2$ | STB | 143.6 | 176.3 | 54.0, 55.1 | 2.11, 2.12 | 2.15, 2.17, 2.42, 2.70 | 16 |
| $Me_2Sn(Oxin)_2$ | *cis* | 110.7 | – | 73.4, 73.7 | 2.15, 2.17 | 2.10, 2.11 (X = O) | 11 |
|  |  |  |  |  |  | 2.31, 2.38 (X = N) |  |
| Et(n-Pr)Sn(2-MeOxin)$_2$ | STB | 145.2 | 139.3 | 70.2, 70.9 | 2.089, 2.145 | 2.066, 2.066 (X = O) | 17 |
|  |  |  |  |  |  | 2.542, 2.597 (X = N) |  |
| $Me[(Me_3Si)_2CH]Sn(Oxin)_2$ | *cis* | 109.7 |  |  | 2.131, 2.172 | 2.078, 2.107 (X = O) | 12 |
| (*p*-$ClC_6H_4$)(*p*-tolyl)Sn(Oxin)$_2$ | *cis* | 106.8 |  | 74.59 | 2.140, 2.140 | 2.084 (X = O) | 13 |
|  |  |  |  |  |  | 2.322 (X = N) |  |
| $Me_2Sn(S_2COEt)_2$ | STB | 130.1 | 150.31 | 62.49, 63.68 | 2.111 | 2.486, 2.501, 3.088, 3.151 | 18 |
| $Me_2Sn(S_2CNMe_2)_2$ | STB | 136 | 149.1 | 63.5, 65.1 | 2.13, 2.16 | 2.497, 2.515, 2.954, 3.061 | 19 |
| $Me_2Sn(S_2CNEt_2)_2$ |  |  |  |  |  |  |  |
| (monoclinic) | { STB | 136.9 | 149.3 | 64.1, 64.6 | 2.12, 2.15 | 2.512, 2.524, 2.932, 3.004 | 20 |
|  | STB | 142.8 | 146.8 | 64.6 | 2.13 | 2.520, 2.947 |  |
| (triclinic) | STB | 142.3 | 147.7 | 64.6, 65.0 | 2.103, 2.133 | 2.518, 2.536, 2.918, 2.969 | 20 |
| (orthorhombic) | STB | 135.6 | 149.20 | 63.43, 65.46 | 2.109, 2.123 | 2.488, 2.515, 2.938, 3.054 | 21 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $Me_2Sn[S_2CN(CH_2)_4]_2$ | STB | 137.3 | 144.88 | 65.43 | 2.112 | 2.518, 2.938 | 22 |
| $n\text{-}Bu_2Sn[S_2CN(C_4H_8)O]_2$ | STB | 141 | | | | | 23 |
| $Ph_2Sn(S_2CNEt_2)_2$ | *cis* | 101.4 | – | 67.6, 67.6 | 2.173, 2.180 | 2.548, 2.613, 2.637, 2.790 | 14 |
| $Me_2Sn(S_2PMe_2)_2$ | STB | 122.6 | 142.3 | 68.9 | 2.132 | 2.482, 3.334 | 24 |
| $Me_2Sn(S_2PO_2C_2Me_4)_2$ | STB | 133.9 | 134.68 | 70.68 | 2.116 | 2.495, 3.130 | 25 |
| $Ph_2Sn[S_2P(OEt)_2]_2$ | STB | 135 | 136.9 | 69.2, 69.7 | 2.10, 2.12 | 2.48, 2.49, 3.20, 3.23 | 26 |
| $Ph_2Sn[S_2P(O\text{-}i\text{-}Pr)_2]_2$ | *trans* | 180 | 103.97 | 76.03 | 2.145 | 2.678, 2.689 | 8 |
| $Me_2Sn(S_2AsMe_2)_2$ | STB | 121.8 | 139.18 [g] | 70.26 [g] | 2.108 | 2.471, 3.515 | 27 |
| $[MeOC(O)(CH_2)_2]_2SnCl_2$ | *cis*-$Cl_2$ | 96.3 | – | 73.3, 74.0 | 2.124, 2.127 | 2.520, 2.524 (X = O) | [b] |
| | | (R = Cl) | | | | 2.401, 2.409 (X = Cl) | |
| $[NH_2C(O)(CH_2)_2]_2SnCl_2$ | *cis*-$Cl_2$ | 95.5 | – | 78.0, 78.7 | 2.059, 2.190 | 2.321, 2.327 (X = O) | [b] |
| | | (R = Cl) | | | | 2.460, 2.464 (X = Cl) | |
| $[EtOC(O)CH_2CH(CO_2Et)]_2SnBr_2$ | | | | | | | |
| low m.p. isomer | *cis*-$Br_2$ | 99 | – | 72, 72 | 2.26, 2.26 | 2.44, 2.46 (X = O) | [c] |
| | | (R = Br) | | | | 2.516, 2.588 (X = Br) | |
| high m.p. isomer | *cis*-$Br_2$ | 101 | – | 72 | 2.24 | 2.49 (X = O) | [d] |
| | | (R = Br) | | | | 2.504 (X = Br) | |
| $Ph_2Sn[3\text{-}(2\text{-}py)\text{-}2\text{-}C_4H_2S]_2$ | *cis* | 101.9 | – | 70.3 | 2.179 | 2.163 (X = C) | [e] |
| | | | | | | 2.560 (X = N) | |
| $n\text{-}Bu_2Sn(5\text{-}NO_2\text{-}2\text{-}SPy)_2$ | STB | 129.2 | 151.2 [g] | 59.5 [g] | 2.162 | 2.477 (X = S) | 28 |
| | | | | | | 2.77 (X = N) | |
| $Me_2Sn(2\text{-}SPyO)_2$ | STB | 138.9(2) | 136.7(1) | 72.0(1) | 2.106(6) | 2.536(1), 2.566(1) (X = S) | [f] |
| | | | | 73.5(1) | 2.128(7) | 2.356(3), 2.410(4) (X = O) | |

[a] acac = acetylacetonate; dbzm = dibenzoylmethanate; trop = tropolonate; Oxin = 8-hydroxyquinolinate; 2-MeOxin = 2-methyl-8-hydroxyquinolinate; 3-(2-py)-2-$C_4H_2S$ = 3-pyridyl-2-thienyl; 2-SPy = 2-pyridinethiolate. [b] P.G. Harrison, T.J. King and M.A. Healy, J. Organomet. Chem., 182 (1979) 17. [c] M. Yoshida, T. Ueki, N. Kasai, M. Kakudo, I. Omae, S. Kikkawa and S. Matsuda, Bull. Chem. Soc. Japan, 41 (1968) 1113. [d] Y. Kumura, T. Ueki, N. Yasuoka, N. Kasai and M. Kakudo, Bull. Chem. Soc. Japan, 42 (1969) 2479. [e] V.G. Kumar Das, J.M.T. Lo, Chen Wei and T.C.W. Mak, Organometallics, 6 (1987) 10. [f] This work. [g] Calculated from the atomic coordinates.

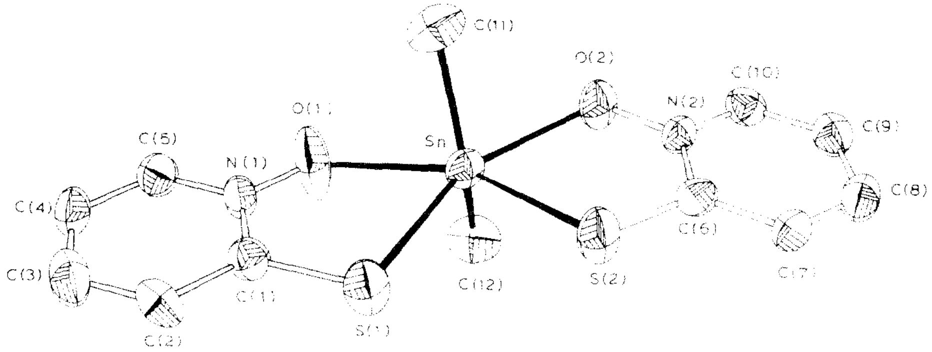

Fig. 1. Molecular structure of dimethylbis(2-pyridinethiolato-*N*-oxide)tin, with labeling and with thermal ellipsoids drawn at 35% probability level.

this distortion, a two-fold axis would pass through Sn and the mid-point of the line joining C(11) and C(12), and this would involve an overall molecular symmetry of $C_{2v}$. The plane comprising the tin and the four donor atoms [O(1), O(2), S(1) and S(2)] is flat (rms = $13 \times 10^{-3}$ Å). The planes containing the atoms of the 2-SPyO ligands are approximately coplanar with this plane (Table 4).

In the idealized case of a six-coordinated diorganotin bischelate, the carbon–tin–carbon angle is 90° for the *cis* and 180° for the *trans* isomer. The angle of 138.9(2)° found for the title compound is close to the average of the two extremes. Table 5 gives a list of reported structural data for diorganotin bischelates and also includes data on three compounds in which the organic group attached to the tin carries a donor site capable of intramolecular coordination. If these three compounds as well those adopting unambiguous *cis* or *trans* geometries are left out of consideration, the C–Sn–C angles for the remainder fall in the range 122.6–156.9°. These latter structures have been generally labeled as 'distorted *trans*' structures, but no convincing reasons have been advanced for the gross deviations from idealized geometry. Table 5 also shows that the Sn–B bond lengths are normal, but the Sn–A bonds are much longer than the bonds normally found in, for example, four- or five-coordinate organotin compounds [33,34].

The geometry of the coordination polyhedron around the tin in $Me_2Sn(2\text{-}SPyO)_2$ is best described as a skew-trapezoidal bipyramid (STB). A schematic representation

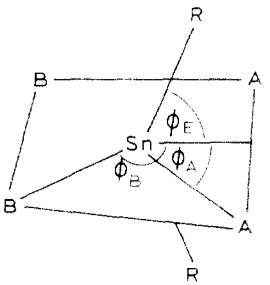

Fig. 2. Schematic representation of the skew-trapezoidal bipyramidal geometry for $R_2Sn(A\text{–}B)_2$ compounds: $\phi_A = 1/2$(angle A–Sn–A), $\phi_B = 1/2$(obtuse angle B–Sn–B), $\phi_E = 1/2$(angle R–Sn–R).

Table 6

Normalized bite and other repulsion-energy parameters for diorganotin bischelates

| $R_2Sn(chelate)_2$ | $b$ | $\phi_A$ | $\phi_B$ | $\phi_E$ | (M–A)/(M–B) | ref. |
|---|---|---|---|---|---|---|
| $Me_2Sn[MeC(O)N(H)O]_2 \cdot H_2O$ | 1.17 | 73.4 | 144.8 | 78.4 | 1.12 | 10 |
| | 1.17 | 73.1 | 144.7 | 78.4 | 1.11 | |
| $Me_2Sn[MeC(O)N(Me)O]_2$ | 1.17 | 72.0 | 143.4 | 72.9 | 1.12 | 15 |
| $Me_2Sn(NO_3)_2$ | 0.92 | 88.2 | 142.7 | 71.8 | 1.18 | 16 |
| Et-n-PrSn(1-MeOxin)$_2$ [a] | 1.17 | 69.6 | 140.2 | 72.6 | 1.24 | 17 |
| $Me_2Sn(S_2COEt)_2$ | 1.06 | 75.2 | 138.8 | 65.0 | 1.25 | 18 |
| $Me_2Sn(S_2CNMe_2)_2$ | 1.07 | 74.6 | 138.8 | 68.0 | 1.20 | 19 |
| $Me_2Sn(S_2CNEt_2)_2$ | | | | | | |
| (monoclinic) | 1.07 | 74.6 | 139.0 | 68.4 | 1.18 | |
| | 1.07 | 73.4 | 138.0 | 71.4 | 1.17 | 20 |
| (triclinic) | 1.08 | 73.8 | 138.6 | 71.2 | 1.16 | 20 |
| (orthorhombic) | 1.08 | 74.6 | 139.0 | 67.8 | 1.20 | 21 |
| $Me_2Sn[S_2CN(CH_2)_4]_2$ | 1.09 | 72.4 | 137.9 | 68.6 | 1.17 | 22 |
| $Me_2Sn(S_2PMe_2)_2$ | 1.16 | 71.2 | 140.0 | 61.3 | 1.34 | 24 |
| $Me_2Sn(S_2PO_2C_2Me_4)_2$ | 1.17 | 67.3 | 138.0 | 67.0 | 1.25 | 25 |
| $Ph_2Sn[S_2P(OEt)_2]_2$ | 1.16 | 68.4 | 137.9 | 67.5 | 1.29 | 26 |
| $Me_2Sn(S_2AsMe_2)_2$ | 1.18 | 69.6 | 139.8 | 60.9 | 1.42 | 27 |
| n-Bu$_2$Sn(5-NO$_2$-2-SPy)$_2$ [a] | 1.00 | 75.6 | 135.1 | 64.6 | 1.12 | 28 |
| Me$_2$Sn(2-SPyO)$_2$ [a] | 1.19 | 68.4 | 141.1 | 69.5 | 0.93 | This work |

[a] Donor atoms of chelate are different.

of this is shown in Fig. 2 for the general case of a skew-trapezoidal bipyramidal bischelate, $[R_2Sn(A\text{–}B)_2]$. The organic R groups can be skewed towards or past the long A–A edge of the trapezium AABB. The stereochemistry can be completely specified [5] by the three angles, $\phi_A$, $\phi_B$ and $\phi_E$ as defined in Fig. 2. An additional useful parameter introduced by Kepert [5] is the normalized bite $b$, a dimensionless quantity obtained by dividing the distance between the donor atoms of the chelate by the average of the metal–donor atom distances. The four parameters for the title compound and for other comparison structures are listed in Table 6. According to the repulsion energy model arguments [4,5], if $b = 2^{1/2}$, the ratio of the unidentate ligand repulsion energy coefficient to the total repulsion energy coefficient for the compound [M(unidentate)$_2$(bidentate)$_2$] has the same value for both *cis* and *trans* octahedral structures. However, for lower normalized bites the above ratio of repulsion energy coefficients increases markedly and is particularly pronounced for the *trans* than the *cis* isomers, except when the *trans* slips into the STB geometry. For the undistorted *trans*-$O_h$ complexes Me$_2$Sn(acac)$_2$ [6] and n-Bu$_2$Sn(dbzm)$_2$ [7], the $b$ values are 1.36 and 1.34, respectively. Table 6 shows that the normalized bite for the title compound (1.19) is somewhat higher than that calculated for other bischelates. The odd entry is $Me_2Sn(NO_3)_2$ ($b = 0.92$); but, the quality of diffraction data for this compound is not high ($R = 0.089$) [16]. A further point arising from Table 6 is that the ratio of the tin–donor atom distances, Sn–A/Sn–B, is greater than unity for all the compounds listed, except for the title compound. For the general case of a *trans*-$[R_2Sn(A\text{–}B)_2]$ octahedral structure in which the donor atoms A, B of the chelating ligand are similar, the bond from tin to the negatively-charged B end is expected to be shorter than the dative Sn–A bond. This would favor skewing of the R groups towards the A–A edge if the normalized bite is small.

Whereas, as a first approximation, nitrogen and oxygen may be considered to be similar, the combination S,N or S,O, with widely differing electronegativities and 'hardness' ($C_B$ for sulfur is higher than that for oxygen or nitrogen [35]), may be expected to introduce some imbalance in the Sn–A/Sn–B ratio. Thus, the Sn–S bonds [2.536(1) and 2.566(1) Å] in the title compound are not unexpectedly longer than the Sn–O bonds [2.414(4) and 2.356(3) Å], but it is noteworthy that the latter bonds are ca. 0.2 Å longer than the Sn–O bonds in the *trans*-[$SnR_2$] octahedral complexes, $Me_2SnCl_2 \cdot 2PyO$ (2.251 Å) [36] and [$Me_2SnCl_2 \cdot 2,6\text{-}Me_2PyO$]$_2$ (2.289 Å) [37], in accord with the proposed STB geometry for the title compound. For the compound n-$Bu_2Sn(5\text{-}NO_2\text{-}2\text{-}SPy)_2$ for which a distorted tetrahedral structure has been suggested [28], the Sn–N bond (2.77 Å) is longer than the Sn–S bond (2.477 Å) (Table 5). A closer examination of structural data suggests that an STB description would be more appropriate. This is borne out by the angular values $\phi_A$, $\phi_B$ and $\phi_L$ for the compound as well as by the sum of the angles at tin in the trapezoidal plane (360.1°). The long Sn–N bonds are readily explicable in terms of ring strain effects in the four-membered chelate ring of the structure and, additionally, as a result of the low degree of covalent character of the Sn–N bond [38]. Coordinate Sn–N bonds of comparable length have been previously described in the literature for $Ph_3Sn(4\text{-}SPy)$ (2.62 Å) [39], $MeSn(CH_2CH_2CH_2)_3N$ (2.62 Å) [40], ($Ph_2SnCl_2 \cdot$ pyrazine)$_n$ (2.782, 2.965 Å) [41] and ($p$-$MeC_6H_4$)Sn[3-(2-pyridyl)-2-thienyl] (2.841 Å) [42].

### *NMR spectra*

The $^2J(^{119}Sn\text{–}C\text{–}^1H)$ value for the title compound in $CDCl_3$ is 82.5 Hz, a value intermediate between values recorded for *cis*-$Me_2Sn(Oxin)_2$ (68.7 Hz) [1] and *trans*-$Me_2Sn(acac)_2$ (99.3 Hz) [43]. A monodentate bonding mode for (2-SPyO) in solution could be ruled out since the coupling constant is unchanged in the presence of added pyridine. The predicted C–Sn–C angle from the measured $^1J(^{119}Sn\text{–}^{13}C)$ value of 698.2 Hz is 139.0°. Thus, the $C_2Sn$ skeletal configuration, and by inference, the skew-trapezoidal geometry, apparently survives in solution. Similar retention of stereochemistry of the $Me_2Sn$ skeleton has been observed for $Me_2Sn(S_2CNEt_2)_2$, for which the $^1J$ values in solution and in the solid state are 664 and 675 Hz, respectively [22]. In contrast, the triphenyl-, tricyclohexyl- and tribenzyl-tin derivatives of 2-pyridinethiol-*N*-oxide are considered to be tetrahedral in $CDCl_3$.

### *Mössbauer spectra*

The tin-119m Mössbauer quadrupole splitting of the title compound is 3.29 mm $s^{-1}$. In the simple point charge approximation, the electric field gradient at tin is generated solely by the organic groups and the efffects of the other electronegative atoms are neglected [2]. The predicted C–Sn–C angle is 136.0°, compared to the observed value of 138.9(2)°. A *cis* configuration has been predicted for $Ph_2Sn(2\text{-}SPyO)_2$ (quadrupole splitting = 1.45 mm $s^{-1}$) [44]; clearly, the combined effect of the bulk of the phenyl group and small bite angle forces this compound to adopt the energetically favored *cis* configuration. The calculated density of 1.754 gm $cm^{-3}$ for the title compound is high compared to that of other diorganotin bischelates of comparable elemental composition and molecular weight, but the momomericity of $Me_2Sn(2\text{-}SPyO)_2$ was established by the slope of the variable-temperature plot. $a$ $-1.96 \times 10^{-2}$ $K^{-1}$, which is in the region expected for monomeric organotins [45].

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