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Crystal structure of tribenzyl(2-pyridinethiolato-*N*-oxide)tin(IV): a rare example of a square pyramidal organotin(IV) compound

Seik Weng Ng [a], **Chen Wei** [b], **V.G. Kumar Das** [b]*

[a] *Institute of Advanced Studies and* [b] *Department of Chemistry, University of Malaya, 59100 Kuala Lumpur (Malaysia)*

and Thomas C.W. Mak *

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories (Hong Kong)

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Abstract

Tribenzyl(2-pyridinethiolato-*N*-oxide)tin(IV), $[(C_6H_5CH_2)_3Sn(2\text{-}SC_5H_4NO)]$, crystallizes in space group $P\bar{1}$, with *a* 9.169(2), *b* 10.498(3), *c* 13.511(4) Å, α 91.54(2), β 104.61(2), γ 112.49(2)° and $Z = 2$. The structure has been refined to $R = 0.028$ using 4593 observed Mo-K_α reflections. The molecule adopts a configuration displaced 91% from a trigonal bipyramid to a square pyramid along the Berry pseudorotation pathway. The basal plane is composed of the oxygen and sulfur atoms of the chelating 2-pyridinethiolato ligand and the carbon atoms of two benzyl groups [Sn–O 2.261(2), Sn–S 2.577(1), Sn–C 2.189(3), 2.196(3) Å]. The apical tin–carbon bond [Sn–C 2.167(3) Å] is shorter than the other two tin–carbon bonds. The tin atom is displaced 0.64(1) Å from the basal plane in the direction of the apical carbon [sum of the basal angles = 341.7(4)°] and the C_{apical}–Sn–L_{basal} angles are in the range 100.1(1)–110.1(1)°. The unusual geometry of tribenzyl(2-pyridinethiolato-*N*-oxide)tin(IV) provides the first example of polytopal dominance of the square-pyramidal configuration in pentacoordinated organotin compounds.

Introduction

Although there have been several reports of pentacoordinated triorganotin(IV) chelates, only the following have been crystallographically authenticated: trimethyltin- [1] and triphenyltin- [2] *N*-benzoyl-*N*-phenylhydroxamates, triphenyltin-1,3-diphenylpropane-1,3-dionate [3], triphenyltin-quinoline-8-thiolate [4] and triphenyltin 2-(2-hydroxy-5-methylphenyl)azobenzoate [5]. The tin atom in each structure is in a trigonal bipyramidal (TBP) environment, with the donor atoms of the chelating ligand spanning one equatorial and one axial site, thereby forcing one of the three tin-bound organic groups into an axial position. The alternative chain structure involving intermolecular chelation of the ligand, such as observed in tribenzyl- [6] and other triorganotin [7] carboxylates, is not adopted in the five examples even though such a bonding mode would allow the attainment of the preferred axially-most-electronegative configuration. The latter configuration which is general for pentacoordinated triorganotin structures, has recently been shown to prevail as well in TBP structures of tetraorganotin triptych compounds such as $[CH_3Sn(CH_2CH_2CH_2)_3N]$ [8]. The internally-coordinated compound, [3-(2-pyridyl)-2-thienyl]tri(*p*-tolyl)tin, on the other hand, adopts a geometry intermediate between tetrahedral and TBP [9]. This intermediate geometry is also found in, for example, the triorganotin derivatives of dithiocarbamic [10] and substituted benzoic [11,12] acids. The tendency to achieve higher-than-four coordination at tin in these compounds is moderated by the dictates of strain in the four-membered rings, (E = O, S).

and by steric and electron-pair repulsion terms. Such compounds are best described as 'pseudo-pentacoordinated', and they must be distinguished from 'true' pentacoordinate structures whose geometries deviate significantly from idealized TBP. A particularly facile distortional mode which has been well-documented for pentacoordinated cyclic phosphoranes [13] and silicates [14–16] is the Berry intramolecular ligand exchange coordinate [17] involving the TBP and square pyramid (SP) as the extreme geometries. The Berry mechanism reflects the intrinsic non-rigidity of these two representative geometries, and indeed, the SP is simply an intermediate state in the interchange of axial and equatorial groups of the dominant TBP polytype.

Although the SP geometry was hitherto unknown among organotin compounds, crystallographic evidence for it exists for the inorganic structures, K_2SnO_3 [18], $SnTa_2O_7$ [19] and $[(CH_3)_4N]^+[(C_7H_6S_2)_2SnCl]^-$ [20]. Holmes and co-workers have reported a quantitative assessment of the distortion of the TBP towards SP geometry for cyclic phosphoranes and silicates using the criteria of dihedral angles [13–16]. The dihedral angle δ_{ij} is the angle between the normals to the TBP faces that have the common edge *ij*, and is the one most intimately associated with the Berry exchange coordinate. This dihedral angle has a value of 53.1° for an idealized TBP but becomes 0° as the edge *ij* disappears on forming the SP.

We have used the above criteria to evaluate the crystallographic data for tribenzyl(2-pyridinethiolato-*N*-oxide)tin(IV) and to demonstrate that it exists in a unique SP configuration. A preliminary report describing this result has appeared [21].

Experimental

Synthesis

Tribenzyltin chloride (4.27 g, 10.0 mmol) was added to an aqueous solution of sodium 2-pyridinethiolate *N*-oxide (a 35% solution supplied by Tokyo Kasei, Japan; 4.5 g, approx. 10 mmol) and the minimum amount of ethanol was added to dissolve the reactants. The mixture was briefly stirred and the product was precipitated by

Table 1

Analytical data (Found (calc) (%)) for organotin 2-pyridinethiolato-*N*-oxides and tribenzyltin compounds

	M.p. (°C)	C	H	N
$(C_6H_5)_3Sn(2\text{-}SPyO)$	113–114	58.00 (58.02)	3.96 (3.99)	2.87 (2.94)
$(C_6H_5CH_2)_3Sn(2\text{-}SPyO)$	93– 94	59.77 (60.27)	4.86 (4.83)	2.67 (2.70)
$(c\text{-}C_6H_{11})_3Sn(2\text{-}SPyO)$	92– 93	55.55 (55.90)	7.53 (7.49)	2.85 (2.84)
$(C_6H_5CH_2)_3SnSC(S)N(CH_3)_2$	94– 95	56.27 (56.28)	5.35 (5.28)	2.74 (2.74)
$(C_6H_5CH_2)_3SnCl\cdot(C_6H_5)_3AsO$	138–139	61.71 (62.47)	4.81 (4.80)	

Table 2

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

Molecular formula	$C_{26}H_{25}NOSSn$
Molecular weight	518.24
Crystal size	$0.34 \times 0.32 \times 0.22$ mm^3
No. of reflections for lattice parameters	21
Cell constants	a 9.169(2) Å α 91.54(2)° b 10.498(3) Å β 104.61(2)° c 13.511(4) Å γ 112.49(2)° V 1151.6(5) Å^3, $Z = 2$ $F(000) = 523.94$
Density (exptl)	1.51 g cm^{-3} (flotation in KI/H_2O)
Density (calcd)	1.495 g cm^{-3}
Space group	$P\bar{1}$
Standard reflections	(212), (301)
Intensity variation	±1%
R_{int} (from merging equivalent reflections)	0.010
Absorption coefficient	12.16 cm^{-1}
Mean μr	0.17
Transmission factors	0.723 to 0.854
Scan mode and rate	$\omega - 2\theta$; 2.02–8.37 deg min^{-1}
Scan range	1° below K_{α_1} to 1° above K_{α_2}
Background counting	stationary counts for one-half of scan time at each end of scan
$2\theta_{max}$	52°
$h\ k\ l$	$0 \leq h \leq 11$, $-13 \leq k \leq 12$, $-17 \leq l \leq 16$
Unique data measured	4916
Observed data with $\lvert F_o \rvert > 3\sigma(\lvert F_o \rvert)$, n	4593
Number of variables, p	271
$R = \Sigma \lVert F_o \rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$	0.028
Weighting scheme	$w = [\sigma^2(F_o) + 0.0005 \lvert F_o \rvert^2]^{-1}$
$wR = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / \Sigma w \lvert F_o \rvert^2]^{1/2}$	0.035
$S = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2/(n-p)]^{1/2}$	1.140
$(\Delta/\sigma)_{max}$	0.002
Residual extremes in final difference map	+0.72 to −0.54 e Å^{-3}

adding water. Single crystals suitable for X-ray diffraction were obtained by recrystallization from chloroform. Other organotin derivatives of the ligand were similarly prepared, although $[(CH_3)_2Sn(2\text{-}SPyO)_2]$ (2-SPyO = anion of 2-pyridinethiol-*N*-oxide) was the unexpected product in the reaction of stoichiometric amounts of the ligand and trimethyltin chloride. For comparison, three additional tribenzyltin compounds, namely the adduct $[(C_6H_5CH_2)_3SnCl \cdot (C_6H_5)_3AsO]$, the dithiocarbamate $[(C_6H_5CH_2)_3SnSC(S)N(CH_3)_2]$ and the acetylacetonate $[(C_6H_5\text{-}CH_2)_3Sn(CH_3C(O)CHC(O)CH_3)]$, were prepared by conventional methods [22]. The analytical data for the compounds (obtained by the Microanalytical Service, University College, London (UK)) along with their decomposition temperatures, are listed in Table 1.

Physical measurements

X-Ray crystallography

Diffraction measurements were made on a Nicolet R3m four-circle diffractometer (graphite-monochromatized Mo-K_α radiation, λ 0.71079 Å), and determination

Table 3

Fractional atomic coordinates ($\times 10^5$ for Sn and S, $\times 10^4$ for O, N and C atoms) and equivalent isotropic temperature factors [a] (Å$^2 \times 10^4$ for Sn and S, $\times 10^3$ for O, N and C atoms)

Atom	x	y	z	U_{eq} [a]
Sn	6060(2)	1820(2)	19989(1)	338(1)
S	−20317(9)	342(8)	6582(6)	529(3)
O	−982(2)	−2100(2)	1439(2)	46(1)
N	−2617(3)	−2487(2)	1209(2)	41(1)
C(1)	−3296(3)	−1589(3)	827(2)	43(1)
C(2)	−5010(4)	−2058(4)	611(3)	57(1)
C(3)	−5931(4)	−3355(4)	787(3)	69(2)
C(4)	−5187(4)	−4227(4)	1187(3)	69(2)
C(5)	−3517(4)	−3766(3)	1395(3)	55(1)
C(6)	1887(4)	2250(3)	1597(3)	54(1)
C(7)	1390(3)	3344(3)	1928(2)	41(1)
C(8)	387(4)	3818(3)	1210(2)	49(1)
C(9)	−38(4)	4869(3)	1508(3)	60(1)
C(10)	471(5)	5455(3)	2500(3)	69(2)
C(11)	1442(5)	4994(3)	3237(3)	71(2)
C(12)	1891(4)	3941(3)	2946(3)	59(1)
C(13)	2482(3)	−673(3)	2209(2)	44(1)
C(14)	4128(3)	451(3)	2731(2)	41(1)
C(15)	5203(4)	1138(3)	2169(3)	53(1)
C(16)	6711(4)	2214(4)	2651(3)	69(2)
C(17)	7166(4)	2625(4)	3691(4)	79(2)
C(18)	6118(5)	1948(5)	4259(3)	81(2)
C(19)	4621(4)	871(4)	3787(3)	59(1)
C(20)	37(4)	392(3)	3441(2)	48(1)
C(21)	−1111(4)	−934(3)	3685(2)	43(1)
C(22)	−569(4)	−1939(3)	4074(2)	55(1)
C(23)	−1629(6)	−3162(4)	4280(3)	74(2)
C(24)	−3279(6)	−3439(4)	4097(3)	84(2)
C(25)	−3842(5)	−2450(5)	3720(3)	79(2)
C(26)	−2766(4)	−1211(4)	3511(3)	57(1)

[a] Equivalent isotropic U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor.

of crystal class, orientation matrix and accurate unit-cell parameters were performed according to established procedures [23a]. Intensities were recorded at 22° C, and data collection and processing parameters are summarized in Table 2. Application of absorption corrections was based on a pseudo-ellipsoidal fit to azimuthal scans of selected strong reflections over a range of 2θ values [23b,23c]. The intensities were processed by the learned-profile procedure [23d]. Structure solution was accom-

Table 4

Molecular dimensions (bond lengths (Å), angles (°)) of tribenzyl(2-thiolatopyridine-*N*-oxide)tin (with standard deviations in parentheses)

Sn-S	2.577(1)	Sn-O	2.261(2)
Sn-C(6)	2.196(3)	Sn-C(13)	2.189(3)
Sn-C(20)	2.167(3)	S-C(1)	1.716(3)
O-N	1.342(3)	N-C(1)	1.362(4)
N-C(5)	1.350(4)	C(1)-C(2)	1.402(4)
C(2)-C(3)	1.366(5)	C(3)-C(4)	1.383(6)
C(4)-C(5)	1.366(5)	C(6)-C(7)	1.485(5)
C(7)-C(8)	1.400(4)	C(7)-C(12)	1.381(4)
C(8)-C(9)	1.383(6)	C(9)-C(10)	1.347(6)
C(10)-C(11)	1.389(6)	C(11)-C(12)	1.397(6)
C(13)-C(14)	1.491(3)	C(14)-C(15)	1.390(5)
C(14)-C(19)	1.387(4)	C(15)-C(16)	1.387(4)
C(16)-C(17)	1.366(7)	C(17)-C(18)	1.378(6)
C(18)-C(19)	1.379(4)	C(20)-C(21)	1.495(4)
C(21)-C(22)	1.391(5)	C(21)-C(26)	1.386(5)
C(22)-C(23)	1.368(5)	C(23)-C(24)	1.380(7)
C(24)-C(25)	1.382(7)	C(25)-C(26)	1.386(5)
S-Sn-O	72.9(1)	S-Sn-C(6)	88.0(1)
O-Sn-C(6)	147.4(1)	S-Sn-C(13)	140.4(1)
O-Sn-C(13)	79.0(1)	C(6)-Sn-C(13)	101.8(1)
S-Sn-C(20)	102.0(1)	O-Sn-C(20)	100.0(1)
C(6)-Sn-C(20)	109.9(1)	C(13)-Sn-C(20)	110.1(1)
Sn-S-C(1)	97.0(1)	Sn-O-N	116.7(2)
O-N-C(1)	120.0(2)	O-N-C(5)	117.2(3)
C(1)-N-C(5)	122.8(2)	S-C(1)-N	119.0(2)
S-C(1)-C(2)	124.0(3)	N-C(1)-C(2)	117.0(3)
C(1)-C(2)-C(3)	120.6(4)	C(2)-C(3)-C(4)	120.5(3)
C(3)-C(4)-C(5)	118.6(3)	N-C(5)-C(4)	120.5(3)
Sn-C(6)-C(7)	114.9(2)	C(7)-C(8)-C(9)	120.8(3)
C(6)-C(7)-C(12)	122.1(3)	C(8)-C(7)-C(12)	117.1(3)
C(7)-C(8)-C(9)	121.1(3)	C(8)-C(9)-C(10)	121.3(4)
C(9)-C(10)-C(11)	119.2(4)	C(10)-C(11)-C(12)	120.0(3)
C(7)-C(12)-C(11)	121.2(3)	Sn-C(13)-C(14)	109.2(2)
C(13)-C(14)-C(15)	121.0(3)	C(13)-C(14)-C(19)	121.2(3)
C(15)-C(14)-C(19)	117.8(2)	C(14)-C(15)-C(16)	120.9(3)
C(15)-C(16)-C(17)	120.5(4)	C(16)-C(17)-C(18)	119.3(3)
C(17)-C(18)-C(19)	120.6(4)	C(14)-C(19)-C(18)	120.9(3)
Sn-C(20)-C(21)	114.2(2)	C(20)-C(21)-C(22)	121.5(3)
C(20)-C(21)-C(26)	120.7(3)	C(22)-C(21)-C(26)	117.8(3)
C(21)-C(22)-C(23)	121.3(4)	C(22)-C(23)-C(24)	120.6(4)
C(23)-C(24)-C(25)	119.0(4)	C(24)-C(25)-C(26)	120.2(4)
C(21)-C(26)-C(25)	120.9(4)		

Table 5

Least-squares planes and dihedral angles

Least-squares planes [a]

Plane	Atoms in plane	Equation of plane				rms (Å × 10^{3})
		l	m	n	d	
1	S, O, C(6), C(13)	−0.1298	0.2364	0.9630	1.7533	51.6
2	O, N, C(1) – C(5)	0.1105	0.3608	0.9261	1.3066	3.8
3	Sn, O, N	0.0311	−0.1960	0.9801	2.5249	–
4	S, C(6), C(20)	−0.2920	0.9225	0.2523	1.5269	
5	S, O, C(20)	−0.8868	−0.1425	0.4397	1.9521	
6	C(6), C(13), C(20)	0.8192	0.2431	0.5195	2.5266	–
7	O, C(13), C(20)	0.0197	−0.7323	0.6807	2.8601	
8	S, C(6), C(13)	−0.1507	0.2057	0.9669	1.7186	
9	S, O, C(13)	−0.0942	0.2873	0.9532	1.6689	–
10	S, O, C(6)	−0.1658	0.2631	0.9504	1.7648	–
11	O, C(6), C(13)	−0.0890	0.2161	0.9723	1.8395	–
12	C(7)–C(12)	−0.8193	−0.3912	0.4192	−1.1767	5.7
13	C(14)–C(19)	−0.4253	0.9031	−0.0604	−2.4988	3.4
14	C(21)–C(26)	0.1879	0.3762	0.9073	4.3872	3.7

Dihedral angles between planes [b]

Planes	Angles (°)	Planes	Angles (°)	Planes	Angles (°)	Planes	Angles (°)
4–5	76.2	6–8	64.6	5–10	58.2	2–14	4.7
6–7	78.9	5–9	62.5	7–11	59.9	1–12	65.3
8–9	5.7	7–9	64.1	10–11	5.3	1–13	77.8
4–6	83.3	6–11	61.0	2–3	32.8	1–14	20.2
5–7	67.3	4–8	61.5				

[a] Equation of plane 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 $a^{\star}$, y_0 to $c \times a^{\star}$, and z_0 to c. [b] Standard deviation ca. 0.4°.

plished by means of Patterson and Fourier methods. All non-hydrogen atoms in the asymmetric unit were subjected to anisotropic refinement. The hydrogen atoms of the aromatic rings and methylene groups were generated geometrically [d(C–H) fixed at 0.96 Å] and included in structure factor calculations with assigned isotropic thermal parameters. All computations were performed on a Data General Nova 3/12 minicomputer with the SHELXTL system [23e]. Analytic expressions of neutral-atom scattering factors incorporating the real and imaginary components of anomalous dispersion were employed [23f]. Blocked-cascade least-squares refinements [23g] converged to the R indices and other parameters listed in Table 2. Fractional atomic coordinates of the non-hydrogen atoms are given in Table 3, bond distances and angles in Table 4 and dihedral angles and least-squares planes in Table 5; tables of hydrogen coordinates and their temperature factors, structure factors and anisotropic thermal parameters are available from the authors on request.

Mössbauer spectra

These were recorded at 80 K on a Cryophysics Mössbauer spectrometer as described previously [24] and the data are presented in Table 6.

Table 6

^{119m}Sn Mössbauer data [a] for tribenzyltin and related compounds (mm s^{-1})

	IS [b]	QS	Γ_1	Γ_2
$(C_6H_5)_3Sn(2\text{-}SPyO)$	1.15	1.86	1.54	1.49
$(C_6H_5CH_2)_3Sn(2\text{-}SPyO)$	1.32	1.99	0.99	1.00
$(C_6H_5CH_2)_3Sn(2\text{-}SPyO)/C_6H_6$	1.31	1.99	0.94	0.91
$(C_6H_5CH_2)_3Sn(2\text{-}SPyO)/C_5H_5N$	1.32	2.02	1.00	1.00
$(c\text{-}C_6H_{11})_3Sn(2\text{-}SPyO)$	1.45	2.44	0.97	0.96
$(C_6H_5CH_2)_3SnCl$	1.51	3.00	1.15	1.06
$(C_6H_5CH_2)_3SnCl \cdot (C_6H_5)_3AsO$	1.42	3.19	0.93	0.90
$(C_6H_5CH_2)_3SnSC(S)N(CH_3)_2$	1.46	1.94	0.92	0.89
$(C_6H_5CH_2)_3SnOC(CH_3)CHC(O)CH_3$ [c]	1.19	1.23	1.03	1.04

[a] Error ±0.05 mm s^{-1}. [b] Relative to $CaSnO_3$ or $BaSnO_3$. [c] Formulation based on satisfactory ^{1}H NMR spectral integration. This compound was slightly air-sensitive.

NMR spectra

^{1}H NMR spectra were recorded at ambient temperatures in $CDCl_3$ using a JEOL PMX60si NMR spectrometer. The data are given in Table 7 along with the complete proton-decoupled ^{13}C NMR data, which were obtained on a JEOL JMN FX-100 instrument operating at 25.00 MHz, using $CDCl_3$ as solvent and internal lock.

Table 7

NMR data for organotin 2-pyridinethiolato-*N*-oxides and tribenzyltin compounds

^{1}H NMR

Compound	$^2J(^{119}Sn\text{-}C\text{-}^1H)$ (Hz) [a]
$(C_6H_5CH_2)_3Sn(2\text{-}SPyO)$	64.5
$(C_6H_5CH_2)_3Sn(2\text{-}SPyO)$ [c]	66.3
$(C_6H_5CH_2)_3SnCl$	66.3 [b]
$(C_6H_5CH_2)_3SnCl$ [c]	71.3
$(C_6H_5CH_2)_3SnCl$/Quin-*N*-oxide [d]	70.8
$(C_6H_5CH_2)_3SnCl \cdot (C_6H_5)_3AsO$	82.3
$(C_6H_5CH_2)_3SnSC(S)N(CH_3)_2$	67.1

^{13}C NMR

Compound	$^nJ(^{119}Sn\text{-}^{13}C)$ (Hz)	$\delta_{R\text{-}Sn}$ (ppm)	$\delta_{2\text{-}SPyO}$ (ppm)
$(C_6H_5CH_2)_3Sn(2\text{-}SPyO)$	311.3	27.9 (benzyl) 123.4, 127.3, 127.9, 128.2	119.9, 128.5, 136.6, 141.5, 153.8
$(c\text{-}C_6H_{11})_3Sn(2\text{-}SPyO)$	347.9 (C(1))	35.6	119.5, 126.2, 128.7, 137.2, 154.0
	17.1 (C(2))	32.0	
	67.1 (C(3))	30.6	
	- (C(4))	27.2	
$(C_6H_5)_3Sn(2\text{-}SPyO)$	619.1 (*ipso*)	144.5	119.7, 128.1, 128.5, 137.0, 154.1
	46.9 (*ortho*)	136.5	
	61.5 (*meta*)	128.3	
	13.7 (*para*)	128.7	

[a] Chemical shift of the CH_2 group is in the 2.5–2.7 ppm range. [b] Lit.: 66.9 Hz: L. Verdonck and G.P. van der Kelen, J. Organomet. Chem., 5 (1966) 532. [c] In pyridine as solvent. [d] Stoichiometric amounts in $CDCl_3$.

Results and discussion

A stereoview of the title compound with atom labeling is shown in Fig. 1, while Fig. 2 depicts the content of the unit cell. The basic structural form assumed by the discrete molecule is a square pyramid with two benzyl groups occupying the basal plane and the third in the apical position. This is clearly seen from the *trans* basal angles, C(13)–Sn–S and C(6)–Sn–O, which have values of 140.4(1) and 147.4(1)°, respectively. These angles are close to the idealized 150° angle. The four atoms comprising the basal plane are approximately coplanar (rms = 5.16×10^{-2} Å), with the tin atom displaced 0.64(1) Å from this plane in the direction of the apical C(20) atom. The C(20)–Sn–L(basal) angles are in the range 100.1(1)–10.1(1)° (Table 4), relative to the idealized value of 105°. An alternative structure based on a distorted tetrahedron is ruled out by the intramolecular Sn–O bond distance [2.261(1) Å], which is well within the range observed for the pyridine (and quinoline) -*N*-oxide adducts of triorganotins [24–27], and which is also shorter than the Sn–S bond [2.577(1) Å] in the compound. The chelate bite angle is 72.9(1)°; the S–C(1)–N–O fragment [torsional angle = −0.5(3)°] of the five-membered, envelope-shaped chelate ring is virtually planar.

The rigidity of the chelate ring disfavors consideration of a *trans* alignment of the sulfur and oxygen atoms in either SP or TBP geometry. However, an axial-equatorial coordination mode is possible, and this, a priori, might be expected to favor a *cis*-TBP geometry unless a combination of ligand constraints and steric repulsions forces angular slippage to the SP form. That this slippage prevails here is indicated by a quantitative consideration of the TBP ↔ SP distortion along the Berry coordinate. We first consider a TBP configuration at tin, with the C(6) and the electronegative O atoms in the apical positions, as inferred from the C(6)–Sn–O angle of 147.1(1)°, the largest of the C–Sn–O angles. The important dihedral angles $\delta_{C(20),S}$, $\delta_{C(13),C(20)}$ and $\delta_{C(13),S}$ are defined respectively by the pair of planes 4–5, 6–7 and 8–9 (Table 5). For the ideal case, with all metal–ligand distances assumed to be

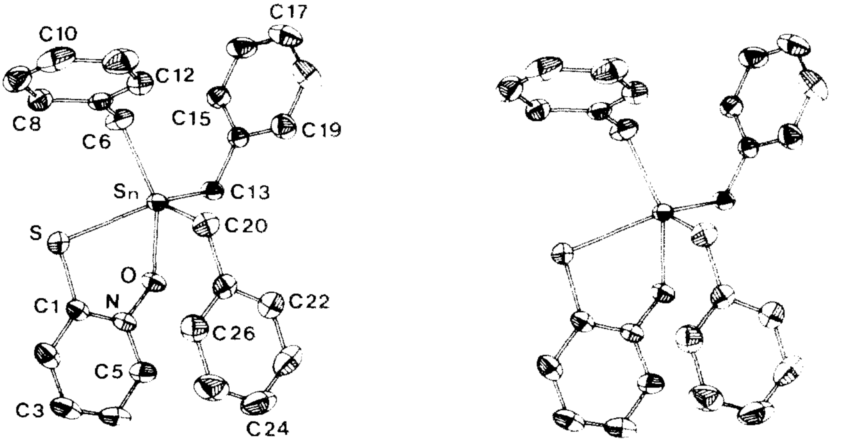

Fig. 1. Molecular structure of tribenzyl(2-pyridinethiolato-*N*-oxide)tin, with atomic labeling and with thermal ellipsoids drawn at 35% probability level.

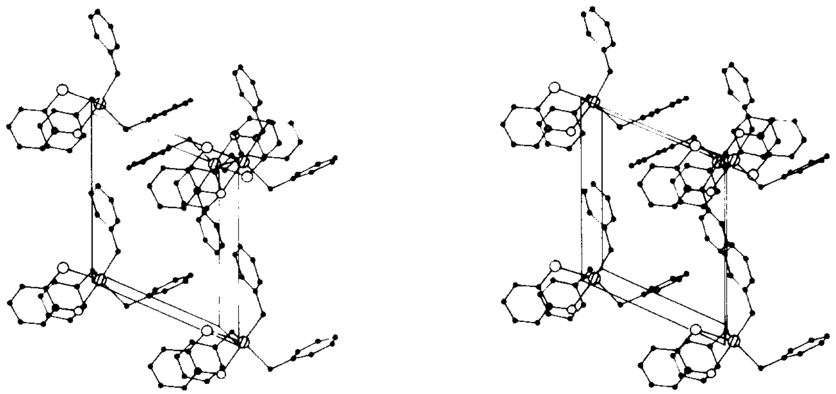

Fig. 2. Packing diagram of tribenzyl(2-pyridinethiolato-*N*-oxide)tin. The origin of the unit cell lies at the lower left corner, with *a* pointing from left to right at a downward slant, *b* upward, and *c* towards the reader.

equal, these three dihedral angles are all 53.1° [28]. In the title compound, the respective angles are 76.2(4) 78.9(4) and 5.7(4)°. Thus, the dihedral angles argue against a TBP geometry. In the isomeric possibility with the S and C(13) atoms at the apical positions [C(13)–Sn–S 140.4(1)°], a similar set of dihedral angles can be defined which yields calculated values of 83.3(4), 67.3(4) and 5.3(4)°. The first set of dihedral angles clearly gives a better fit to the values of 75.7, 75.7 and 0.0° calculated for an ideal SP. With the set of nine dihedral angles [$\delta_{C(20),S}$, $\delta_{C(13),C(20)}$, $\delta_{C(13),O}$, $\delta_{C(20),O}$, $\delta_{C(6),C(20)}$, $\delta_{O,S}$, $S_{C(6),S}$, $\delta_{C(13),O}$, $\delta_{C6),C(13)}$], the calculated percentage displacement [13] towards SP from TBP is 91. This value contrasts with the 77% SP character calculated for the inorganic tin derivative $[(CH_3)_4N]^+[(C_7H_6S_2)_2SnCl]^-$ [20].

The lengths of the Sn–C bonds in the title complex are in good agreement with corresponding values for tetrahedral $[(C_6H_5CH_2)_4Sn]$ [2.18 Å (av.)] [29] and $[(C_6H_5CH_2)_3Sn]_2O$ (2.167 Å) [30] and the five-coordinated TBP compound $[(C_6H_5CH_2)_3SnOC(O)CH_3]$ [2.17 Å (av.)] [6]. The Sn–S bond of 2.577(1) Å, though longer than the Sn–S bonds in $[(C_6H_5)_3Sn]_2S$ (2.370, 2.403 Å) [31], is much shorter than the dative Sn ← S bond in the thiourea adducts of dimethyl- and diphenyltin dichlorides (2.729 and 2.686 Å, respectively) [32]. The N–C_α bonds [1.350(4), 1.362(4) Å] in the title compound are virtually of the same length. The pyridine-*N*-oxide plane is twisted with respect to the Sn–O–N plane by 32.8(3)°, in contrast to the sterically favored, near-orthogonal disposition of these planes in TBP complexes of tin and transition metals with monodentate pyridine (or quinoline) -*N*-oxide ligands [24–27]. The phenyl ring of the apical benzyl group is approximately parallel to the pyridine-*N*-oxide ring [dihedral angle 4.7(4)°] and is 3.321 Å from the pyridyl nitrogen.

The molecules of the title compound are packed in the crystal lattice in such a way as to leave a vacant sixth coordination site opposite to the Sn–C(20) bond, rather reminiscent of the structure of square pyramidal pentaphenylantimony [33]; the shortest intermolecular contacts of tin are Sn · · · Sn′ 5.205 and Sn · · · S′ 4.147 Å, where the primed atoms are at $(-x, -y, -z)$. Although the extent of influence of packing forces on the present structure is unknown, we note that they have been invoked to explain the SP preference of the antimony atom in [K(18-crown-6)][(PhSbI$_2$)$_4$I] [34].

The Mössbauer spectral data for the title compound have been compared with the triphenyl- and tricyclohexyl-tin analogues and with some selected tribenzyltin systems in Table 7. The magnitudes of the isomer shift values of the triorganotin compounds of 2-pyridinethiolato-*N*-oxide are seen to increase in the order $C_6H_5 < C_6H_5CH_2 <$ cyclo-C_6H_{11}, consistent with the σ-donor properties of the organic moieties. The quadrupole splitting (*QS*) values, however, do not permit an unambiguous assignment of the coordination number of tin in these systems. Nevertheless, we are inclined to view the geometry of the tricyclohexyltin derivative as essentially tetrahedral rather than *cis*-TBP by analogy with other tricyclohexyltin systems. The Mössbauer data for the title compound were essentially unchanged when recorded for frozen samples in benzene or pyridine. The *QS* value for $[(C_6H_5CH_2)_3SnCl \cdot (C_6H_5)_3AsO]$ is in the range expected for TBP structures with equatorial locations of the organic groups [35]. The *QS* for the acetylacetonate derivative appears to be extremely small for a *cis*-TBP configuration.

In solution the tribenzyltin compounds appear to be essentially four-coordinate except for the adduct $[(C_6H_5CH_2)_3SnCl \cdot (C_6H_5)_3AsO]$, as deduced from their ^1H NMR spectra compared to the spectrum of $[(C_6H_5CH_2)_3SnCl]$. The $^2J(^{119}Sn-C-^1H)$ value of 66.3 Hz in the parent $[(C_6H_5CH_2)_3SnCl]$ is raised to ca. 71 Hz in pyridine, but this solvent exerts little change on the title compound. The ^{13}C NMR data for the title compound and of related derivatives confirm this finding. Thus only one benzylic carbon signal is observed, instead of the two expected if either a *cis*-TBP or an SP geometry were retained in solution. Indeed, the ^{13}C NMR spectrum of the title compound remained unchanged even at $-90\,^\circ C$. The magnitude of $^1J(^{119}Sn-^{13}C)$ is 311.3 Hz, much smaller than that of 429.1 Hz recorded for the adduct $[(C_6H_5CH_2)_3SnCl \cdot (C_6H_5)_3AsO]$. For the triphenyltin analogue, the ^1J of 619.1 Hz similarly implies a four-coordinated tin environment in solution; cf. 614.3 Hz for $[(C_6H_5)_3SnCl]$ [36].

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