

Preliminary communication

First example of polytopal dominance of square pyramidal geometry in organotin pentacoordination: crystal structure of tribenzyl(2-thiolatopyridine-*N*-oxide)tin(IV)

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Abstract

The coordination geometry about the central atom in monomeric tribenzyl(2-thiolatopyridine-*N*-oxide)tin(IV) is a unique square pyramid, with one benzyl carbon atom occupying the apical position and the basal plane containing the other two benzyl carbon atoms along with the oxygen and sulfur atoms of the chelating ligand; the tin atom is displaced out of the basal plane in the direction of the apical carbon atom by 0.64(1) Å.

Although the limiting geometries in pentacoordination, namely the trigonal bipyramid (TBP) and the square pyramid (SP), are close in energy [1] and readily interconvertible by the Berry mechanism [2,3 *] (see Fig. 1), the SP geometry is rarely encountered in non-transition metal systems [4] and, in the case of tin, has been observed only for the inorganic derivatives K₂SnO₃ [5], SnTa₂O₇ [6] and [Me₄N]⁺ [(C₇H₆S₂)₂SnCl]⁻ [7]. In a general sense, distortions from idealised TBP geometry may be ascribed to movement along the Berry coordinate from TBP to SP, and a quantitative assessment of this is available for cyclic phosphoranes [8] using the criterion of dihedral angles [9 *]. Among pentacoordinated organotin compounds, however, no evidence has previously been reported for significant SP character in the crystallographically studied structures, although the intrinsic non-rigidity of the dominant TBP polytope has been discerned in solution [10–12] and particularly convincingly in the case of Ph₂SnClBr · n-Bu₃PO [13], which undergoes a slow Berry pseudorotation in CH₂Cl₂ at temperatures below –60 °C.

* Reference number with asterisk indicates a note in the reference list.

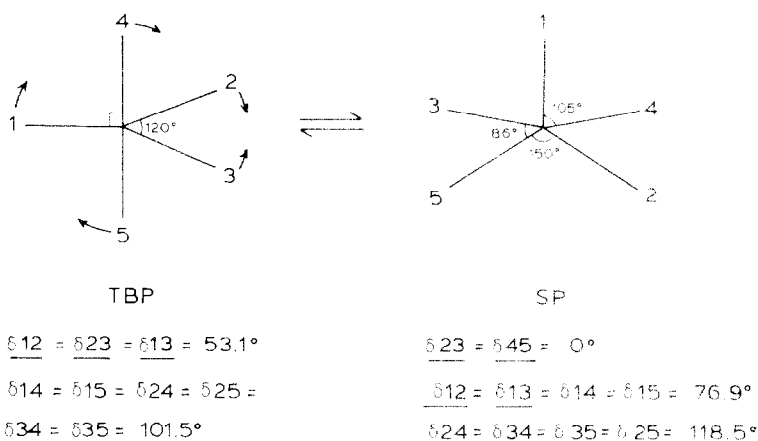


Fig. 1. Idealised geometries related by the Berry interconversion mechanism: TBP = trigonal bipyramidal, SP = square pyramidal. The shape-defining dihedral angles [9], δ_{ij} , are underlined

Our continuing interest in the coordination chemistry and biological properties of triorganotin compounds prompted the present study in which the fungicidal [14] ligand, pyridine-*N*-oxide-2-thiol, was chosen as the chelate functionality bonded to tribenzyltin, among other $R_3\text{Sn}$ units, to yield the title compound **1** [15 *]. The tin-119m Mössbauer spectrum [16 *] of **1** (isomer shift, IS = 1.32; quadrupole splitting, QS = 1.99 mm s⁻¹) is similar to that of the triphenyltin analogue (IS = 1.15, QS = 1.86 mm s⁻¹). The data did not, however, allow unequivocal distinction between a tetrahedral geometry and a *cis*-[SnR₃X₂]TBP geometry [17] for either structure, and this prompted us to undertake an X-ray study on **1**.

Crystal data for **1**: C₂₆H₂₅NOSSn, *M* = 518.2, triclinic, space group $P\bar{1}$, *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)°, *U* 1151.6(5) Å³, *D_c* 1.495 g cm⁻³, *D_m* 1.51 g cm⁻³ for *Z* = 2. A total of 4916 reflections ($2\theta_{\text{max}}$ 52°) was collected on a Nicolet R3m diffractometer with graphite monochromatised-Mo-*K_α* (λ 0.71096 Å) radiation. The structure was solved by the heavy-atom method and refined to a final *R* index of 0.028 for 4593 independent absorption-corrected reflections with $|F_0| > 3\sigma(|F_0|)$ *.

Figure 2 depicts the molecular structure with the atom labelling (35% thermal ellipsoids). The square pyramidal disposition of the ligand groups is evident, with the Sn atom displaced by 0.64(1) Å out of the basal plane (containing S, O, C(13) and C(6)) towards the apical C(20) atom. The apical Sn–C(20) bond is shorter than the basal Sn–C bonds by 0.025 Å (av.); the C(20)–Sn–L (basal ligand atom) angles lie in the range 100.0(1)–110.1(1)°. Substantiating the SP geometry at tin is the set of measured dihedral angles (Fig. 2) specified by the subscript numerals 1–5 which (in terms of the numbering in Fig. 1) represent respectively, C(20), S, C(13), O and C(6). This yields a calculated displacement of 91.1% towards SP along the Berry TBP–SP coordinate for the pentacoordinated structure of the monomeric title

* A table of atomic coordinates and a full list of bond lengths and angles has been deposited with the Cambridge Crystallographic Data Center.

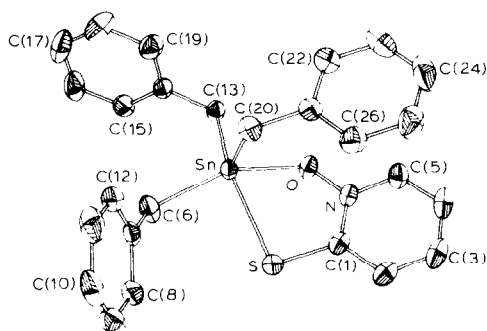


Fig. 2. Molecular structure and labelling scheme for **1**. Important distances (Å) and angles ($^{\circ}$): Sn–C(6) 2.196(3), Sn–C(13) 2.189(3), Sn–C(20) 2.167(3), Sn–O 2.261(2), Sn–S 2.577(1); C(6)–Sn–C(20) 109.9(1), C(13)–Sn–C(20) 110.1(1), C(20)–Sn–O 100.0(1), C(20)–Sn–S 102.0(1), O–Sn–S 72.9(1), Sn–O–N 116.7(2), S–Sn–C(13) 140.4(1), O–Sn–C(6) 147.4(1). Dihedral angles (referenced to numbering scheme of Fig. 1 with 1–5 representing C(20), S, C(13), O and C(6), respectively; standard deviations ca. 0.3°): δ_{45} 5.7, δ_{12} 76.2, δ_{13} 78.9, δ_{14} 67.3, δ_{15} 83.3, δ_{24} 117.5, δ_{25} 118.5, δ_{34} 115.9, δ_{35} 115.4.

compound. Inspection of Fig. 2 also indicates that the residual TBP character in **1** has its origin in a *cis*-[SnR₃X₂] TBP geometry in which the O (rather than the less electronegative S) and C(6) atoms appear to be the likely axial occupants.

The Sn–S and Sn–O bond lengths are in the normal range for higher-than-four coordinated organotin structures, and the S–C(1)–N–O fragment of the envelope-like chelate ring is virtually planar. The pyridine-*N*-oxide plane is twisted with respect to the Sn–O–N plane by $32.8(3)^{\circ}$, in contrast to the sterically favoured, near-orthogonal dispositions of these planes [18] in TBP complexes of tin and transition metals in which the pyridine- and quinoline-*N*-oxide ligands act in the monodentate mode. Presumably, in the present case the high energy constraints of the chelate ring [19 *] and ligand repulsion effects favour angular slippage of the TBP geometry to the SP form. However, packing effects may also be an important consideration.

The molecules 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 situation for square pyramidal pentaphenylantimony [20]; the shortest intermolecular contacts of tin are Sn \cdots Sn' 5.205 and Sn \cdots S' 4.147 Å, where the primed atoms are at $(-x, -y, -z)$.

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- 3 Indeed, the SP is simply an intermediate state in the interchange of axial and equatorial groups of the TBP.

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- 15 Single crystals for X-ray study were obtained by slow evaporation of a chloroform solution of **1** synthesised by treating tribenzyltin chloride with sodium 2-pyridinethiolate *N*-oxide in aqueous ethanol. Anal. Found: C, 59.97; H, 4.86; N, 2.57. $C_{26}H_{23}NOSSn$ calcd.: C, 60.27; H, 4.83; N, 2.70%; m.p. 93–94 °C; NMR ($CDCl_3$): δ (CH_2Ph) 2.6, δ (CH_2Ph) 27.9; $^2J(^{119}Sn-CH_2Ph)$ 66.3, $^1J(^{119}Sn-^{13}CCH_2Ph)$ 311.3 Hz.
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